Characterization of novel fullerene containing polymers

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Characterization of Novel Fullerene Containing Polymers

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ABSTRACT

Fullerene containing poly (*t*-butyl methacrylate) (PtBMA-*b*-C₆₀) with average molecular weights of 8,000 and 14,000 Da (denoted by LFBMA and HFBMA respectively) and fullerene containing poly (methacrylic acid) (PMAA-*b*-C₆₀) with average molecular weights of 12,500 Da (denoted as FPMAA) were synthesized by atom transfer radical polymerization (ATRP). The aggregation behaviour of LFBMA and HFBMA in chlorobenzene-ethyl acetate mixed solvents and FPMAA in aqueous and salt solutions were studied using thermogravimetric analysis (TGA), UV-vis spectroscopy, potentiometric and conductometric titration, laser light scattering (LLS) and transmission electron microscopy (TEM).

PtBMA-*b*-C₆₀ was first dissolved in chlorobenzene (which is a good solvent for both blocks), and ethyl acetate (precipitant) was added to induce its aggregation in the solvent mixtures. Ethyl acetate is a good solvent for homopolymer PtBMA and a poor solvent for C₆₀. It was observed that a critical precipitant composition (CPC) existed where the aggregation of the polymer chains was induced and it decreased with decreasing molecular weight (M_n).

Both dynamic and static light scattering studies (DLS and SLS) were used to characterize the aggregation behavior of LFBMA and HFBMA in various solvent mixtures. In LFBMA-mixed solvent systems, both unimers and aggregates coexisted. The hydrodynamic radius, R_h of the aggregates decreases gradually with the addition of ethyl acetate. In the HFBMA-mixed solvent systems, only aggregates were

present. R_h of the aggregates decreased initially with the addition of ethyl acetate until a critical solvent composition where it increased again.

TEM studies revealed “dimple-like structures” large compound vesicles (LCVs) in LFBMA-mixed solvent systems. Similar aggregates were observed in HFBMA-mixed solvent systems. However, there existed a critical solvent composition in the HFBMA-mixed solvent systems whereby no “dimple-like structures” were observed, and the value of R_g/R_h increased from 0.8 to 1.5.

The aggregation behaviour of PMAA-*b*-C₆₀ in aqueous and salt solutions was examined using potentiometric titration, DLS and TEM. Micelles and large compound micelles (LCMs) coexist in aqueous polymer solutions. During the course of neutralization, micelle size remains constant at ~10 nm, and the LCM size increases from ~90 to ~152 nm. TEM studies revealed fractal pattern at the fully neutralized condition in the presence of salt. In the unneutralized condition, the LCM acts as nuclei for the crystallization of the salt, and no fractal pattern is observed. It is believed that the negatively charges on the surface of LCM play a vital role in the fractal formation.

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LIST OF SYMBOLS

Γ	Decay rate (s^{-1})
τ	Decay time (s)
ν	Frequency (Hz)
θ	Measuring angle (radian)
π	Osmotic pressure (Pa)
AQ	Aqueous solution
C_{60}	Fullerene
CB	Chlorobenzene
CMC	Critical micelle concentration
CPC	Critical precipitant composition
D	Translational diffusion coefficient
DLS	Dynamic light scattering
$\frac{\partial n}{\partial C}$	Specific refractive index increment (ml/g)
E	Electric field (N/C)
EA	Ethyl acetate
FPMAA	PMAA- <i>b</i> - C_{60}
HFBMA	High molecular weight PtBMA- <i>b</i> - C_{60}
k	Boltzmann constant (JK^{-1})
LCM	Large compound micelle
LCV	Large compound vesicle
LFBMA	Low molecular weight PtBMA- <i>b</i> - C_{60}

M_n	Average molecular weight (g/mol)
M_w	Average molecular weight (g/mol)
n	Refractive index of the solvent
N_A	Avogadro constant (mol^{-1})
N_{agg}	Aggregation number
P	Dipole of moment (debye)
$\text{p}K_a$	Dissociation constant
PMAA	Poly (methacrylic acid)
PtBMA	Poly (<i>t</i> -butyl methacrylate)
q	Light scattering vector (m^{-1})
R	Gas law constant (J/mol.K)
R_g	Radius of gyration (nm)
R_h	Hydrodynamic radius (nm)
R_h^{app}	Apparent hydrodynamic radius (nm)
R_θ	Rayleigh ratio
SLS	Static light scattering
η	Solvent viscosity (Pa)
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
λ	Wavelength (nm)
X_{EA}	Molar composition of ethyl acetate
α	Degree of neutraliation

LIST OF PUBLICATIONS

Tan, C. H., Ravi, P., Dai, S. and Tam, K. C. (2004). Solvent Induced Large Compound Vesicles Of Fullerene [60] Containing Poly(*tert*-butyl methacrylate). **Langmuir**. 20, 9882-9884.

Tan, C. H., Ravi, P., Dai, S. and Tam, K. C. (2004). Polymer-Induced Fractal Patterns of Fullerene [60] Containing Poly(methacrylic acid) in Salt Solution. **Langmuir**. 20, 9901-9904.

1.0 INTRODUCTION

1.1 Background

Fullerene (C_{60}) is a single molecule consisting of 60 carbon atoms arranged in a structure of a soccer ball with a hollow centre. It has received extensive attention around the world due to its unique chemical and physical properties since its breakthrough in 1985 [Kroto et al., 1985; Kroto, 1988; Curl and Smalley, 1988]. However, many of its potential applications have been hindered by its poor solubility and processability. Grafting polymer chains onto fullerene is particularly interesting because a combination of fullerene and polymer not only significantly improves the solubility and processability of fullerene, but also directly leads to useful materials. Some progress has been made, resulting in the development of several types of C_{60} -containing polymers, however their solution properties are still not well characterized and is poorly understood [Weis et al., 1995; Sun et al., 1995; Okamura et al., 1997].

These micelle-forming C_{60} containing polymers have spawned a new area of application for fullerenes. It is now possible to improve the processability of fullerene by directly using the C_{60} containing polymers. The self-assembly properties of various block copolymers have attracted significant attention by the scientific community, resulting in the development of new experimental techniques [Alexandridis, 1996; 1997] as well as creating potential applications, e.g. for the construction of controlled release system [Paavola et al., 1998]. This is attributed to growing research interest and focus on developing a fundamental understanding on the aggregation behaviour of the micelles. Similarly, in order to utilise the vast

potential of this unique class of C_{60} containing polymers, fundamental understanding is also required, especially on the solvent effects on the self-assembly behaviour of C_{60} containing polymers. For this reason, C_{60} containing polymers in mixed-solvents, aqueous and salt systems were studied in this project.

This report consists of two parts. The first part will focus on the aggregation behaviour of fullerene containing poly(*t*-butyl methacrylate) (PtBMA-*b*- C_{60}) in chlorobenzene-ethyl acetate mixed solvents. Chlorobenzene is a common solvent for both blocks (C_{60} and PtBMA), that is, it is a good solvent (lyophilic) for both blocks. Ethyl acetate is a good solvent (lyophilic) for PtBMA, but a poor solvent (lyophobic) for C_{60} . The polymer will first be dissolved in the common solvent (chlorobenzene), and precipitant (ethyl acetate) was added to induce the aggregation of the polymer. It will be interesting to study this selective solvent induced micellization of PtBMA-*b*- C_{60} in the chlorobenzene-ethyl acetate mixed solvent systems.

The second part will focus on the aggregation behaviour of fullerene containing polymers in polar solvents. Fullerene containing poly(methacrylic acid) (PMAA-*b*- C_{60}) in aqueous and salt systems. This polymer was obtained through the hydrolysis of fullerene containing poly(*t*-butyl methacrylate) in acidic condition. The aggregation behaviour of this pH responsive water-soluble polymer in aqueous and salt systems will be elucidated. This polymer is hydrophobic and insoluble at low pH. An increase of pH results in the ionization of the carboxylic groups on the polymer backbones enhances its hydrophilicity. This triggers interesting changes in the polymer conformation that leads to the self-assembling of the polymers, which

are controlled by a variety of factors including hydrogen bonding among carboxylic groups, and electrostatic repulsion between ionized carboxylate groups.

1.2 Scope and objectives of this project

The scope and objectives of this project are:

- to study the aggregation behaviour of fullerene containing poly(*t*-butyl methacrylate) in chlorobenzene-ethyl acetate mixed solvents
- to study the aggregation behaviour of fullerene containing poly(methacrylic acid) and aqueous and salt solutions

The experimental techniques used for the polymer characterization are mainly thermogravimetric analysis (TGA), UV-vis spectroscopy, potentiometric and conductometric titration, laser light scattering (LLS) and transmission electron microscopy (TEM).

Thermogravimetric analysis and UV-vis spectroscopy were used to verify the grafting of fullerene onto the polymer chain. The dissociation constant (pK_a) was extracted by careful analysis of the titration curve and the information on the conformational transition during the process of neutralization were obtained. Laser light scattering (LLS) is a technique for studying the transport properties of polymer chains in solution. The hydrodynamic radius (R_h) and the radius of gyration (R_g) of the polymer aggregates were measured by dynamic and static light scattering respectively, thus the particle size and shape of polymer aggregate were elucidated. The morphologies of the aggregates are further confirmed by transmission electron

microscopy. Direct morphological investigation determined by TEM provides images of the aggregates that could be used to validate the microstructure determined from light scattering studies.

1.3 Survey of this report

This thesis has 6 chapters. A brief introduction of the research work is given in Chapter 1. Chapter 2 presents the literature review and Chapter 3 covers the materials and equipments used in this work. Chapter 4 examines the aggregation behaviour of $PtBMA-b-C_{60}$ of two different block lengths in chlorobenzene-ethyl acetate mixed solvents. The self-assembly behaviour of pH responsive water-soluble $PMAA-b-C_{60}$ in aqueous and salt solutions is discussed in Chapter 5. Finally Chapter 6 concludes the report and recommends future studies for the current project.

2.0 LITERATURE REVIEW

2.1 Theoretical Background of Experimental Methods

2.1.1 Theoretical Background of Laser Light Scattering (LLS)

Light scattering could be explained in terms of electromagnetic theory. When a light wave falls on a molecule, the oscillating electric field associated with the wave polarizes the electron clouds of the atoms in the molecules. These oscillating electron clouds serve as a secondary source of light and emit light in different directions. This important idea was suggested about 100 years ago by Lord Rayleigh [Flory, 1953].

With the introduction of coherent laser sources, new experiments were developed. In these experiments, it is possible to record all the temporal variations of the scattered light, which are then subjected to spectral analyses. The temporal variations of the scattered radiation yield the familiar Doppler shift and the broadening of the central Rayleigh line can be used to determine the dynamic properties of the system. Therefore, this technique is often called dynamic light scattering (DLS). The intensity of the scattered light can be analyzed using photon correlation spectroscopy (PCS). From this, the size and shape of macromolecules, as well as molecular interaction can be studied. Since its introduction, laser light scattering has become an important research tool for probing the molecular dynamics of polymer chains.

2.1.1.1 Static Light Scattering (SLS)

Light scattering is a phenomenon of absorption and re-emission of the electromagnetic radiation. In a typical experiment, a dispersion of particles is

illuminated by an incident beam. The direction of propagation of this beam is defined by an incident wave vector $\vec{k}$, with magnitude $k = 2\pi n/\lambda = n\omega_0/c$, where n is the medium refractive index and ω_0 is the circular frequency in vacuum. The radiation scattered under an angle θ with respect to the incident beam is characterized by a scattering wave vector: $\vec{q} = \vec{k}_i - \vec{k}_s$. By taking into account $|k_i| = |k_s|$, the magnitude of $\vec{q}$ can be represented by the expression:

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2.1)$$

For Rayleigh scattering, the intensity of scattered light for a small particle can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \quad (2.2)$$

where α the polarizability of the particle, ϵ_0 the electric permittivity of vacuum. However, when the particle size is greater than $\lambda/20$, (e.g. high molecular weight polymer chain), the Rayleigh scattering is not suitable. In this condition, the light scattered from different points of the particles will reach the detector with different phases. The beams scattered from different points if coherent will lead to the phenomenon called intra-particle interference. Then the scattering intensity could be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} \sum_{i,j=1}^N \exp[iq \cdot (r_i - r_j)] \quad (2.3)$$

For condition when the scattering volume contains several polymer chains, the inter-particle interference also contributes to the scattered intensity. However at low

concentration, polymer chains are sufficiently far apart from each other and the scattering intensity for the dilute polymer solution can be described by,

$$\frac{I_s}{I_i} = \frac{\pi^2 \alpha^2 \sin^2 \theta}{\lambda^4 \epsilon_0^2 r^2} n_p \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.4)$$

where n_p is the number of polymer chains in the scattering volume and the static structure factor $S(q)$ is defined as the summation factor divided by N , the monomer number of the polymer chain.

$$S(q) = \frac{1}{N} \sum_{i,j=1}^N \langle \exp[iq \cdot (r_i - r_j)] \rangle \quad (2.5)$$

The local segment density, which corresponds to the number of monomers per unit volume, is defined as

$$\begin{aligned} \rho(\vec{r}) &= \sum_{m,i} \delta(\vec{r} - \vec{r}_{mi}) \\ \rho &= \langle \rho(\vec{r}) \rangle = n_p N / V \end{aligned} \quad (2.6)$$

where the pair distribution function $\langle \rho(\vec{r}) \rho(0) \rangle$ is called the autocorrelation function of the segment density. The static structure factor is related to the density autocorrelation function by,

$$S(q) = \frac{4\pi}{\rho} \int_0^\infty \langle \rho(\vec{r}) \rho(0) \rangle \frac{\sin qr}{qr} r^2 dr = \frac{N_A N}{CM} \int_V \langle C(\vec{r}) C(0) \rangle \exp(i\vec{q} \cdot \vec{r}) d\vec{r} \quad (2.7)$$

For a polymer chain with any conformation at low angle where $qR_g < 1$ (R_g is the z-averaged radius of gyration), the static structure can be approximated as,

$$S(q) = \frac{N}{1 + q^2 R_g^2 / 3} \quad (2.8)$$

In addition, the $S(q)$ for a Gaussian chain at any scattering angles can be determined from the Debye function $f_D(x)$ as defined by,

$$f_D(x) = 2x^{-2} [1 - x^{-2} (1 - \exp(-x^2))] \quad (2.9)$$

$$S(q) = Nf_D(qR_g) \quad (2.10)$$

The form factor or the internal structure factor $P(q)$ is defined as the ratio of $S(q)$ to $S(0)$. For Gaussian chain $R_g^2 = Nb^2/6$ and

$$P(q) = \frac{S(q)}{S(0)} = \frac{S(q)}{N} = f_D(qR_g) \quad (2.11)$$

For a hard sphere with the radius of R_s , $R_g^2 = 0.6R_s^2$,

$$P(q) = \left[3(qR_s)^{-3} (\sin(qR_s) - (qR_s) \cos(qR_s)) \right]^2 \quad (2.12)$$

While for a rod with rod length of L , $R_g^2 = L^2/12$,

$$P(q) = \frac{2}{qL} \int_0^{qL} \frac{\sin z}{z} dz - \left(\frac{2 \sin(qL/2)}{qL} \right)^2 \quad (2.13)$$

For static light scattering on the polymer solutions, the molecular parameters can be determined from the well-known Zimm Plot as described by equation 2.14,

$$\frac{KC}{R_\theta} = \frac{1}{M_w} \left(1 + \frac{1}{3} q^2 R_g^2 \right) + 2A_2 C \quad (2.14)$$

where $K (=4\pi^2 n^2 (\frac{\partial n}{\partial C})^2 / N_A \lambda^4)$ is an optical constant with N_A , n , and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the light in vacuum, respectively. C is the polymer concentration in gram per milliliter and R_θ is the excess Rayleigh ratio at scattering angle θ . The refractive index increment of the polymer solutions, $(\frac{\partial n}{\partial C})$ can be measured using a differential refractometer. The z-averaged radius of gyration R_g , the second virial coefficient A_2 and the weight average molecular weight M_w can be determined from the above equation by extrapolating to zero concentration and zero angle. Most of this information can be derived by constructing the Zimm plot.

2.1.1.2 Dynamic Light Scattering (DLS)

Dynamic light scattering takes into account the frequency broadening of the scattered light due to the transfer of a small amount of kinetic energy from the incident light. These fluctuations can be caused by either translational diffusion of particle as they move in and out of the scattering volume, or by the rotational motion of non-spherical particles in the scattering volume. Due to the thermal motion, the molecules are constantly moving around and their positions and moment are changing with time. The averaged intensities $\langle I \rangle$ over long observation time T can be expressed by the equation below [Brown, 1993]

$$\langle I(\theta) \rangle = \frac{1}{T} \lim_{T \rightarrow 0} \left(\int_0^T I(\theta, t) dt \right) \quad (2.15)$$

In order to study the dynamic properties of the scattering system, correlation functions need to be obtained from the time dependent measurements. These functions can then be transformed using Fourier transformation techniques to yield appropriate scattering spectra that contain molecular information on the dynamics of the molecules. The appropriate correlation function is described below [Brown, 1993; Akcasu, 1993]:

$$G_2(t) = \langle I(t)I(t + \tau) \rangle \quad (2.16)$$

This function is called autocorrelation function of scattered intensity, and it can be normalized as shown below:

$$g_2(t) = \frac{\langle I(t)I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (2.17)$$

where $I(t)$ is an average value of the product of the scattered intensity at an arbitrary observation time, t , and $I(t + \tau)$ is the intensity registered at decay time τ . The above expression can be simplified using the Siegert relations [Brown, 1993]:

$$G_2(t) = B(1 + \beta \langle g_1(t) \rangle^2) \quad (2.18)$$

$$g_2(t) = 1 + \beta \langle g_1(t) \rangle^2 \quad (2.19)$$

Two other correlation functions can also be obtained:

$$G_1(t) = (G_2(t) - B)^{\frac{1}{2}} \quad (2.20)$$

$$g_1(t) = \sqrt{\frac{G_2(t) - B}{B\beta}} \quad (2.21)$$

where $G_1(t)$ and $g_1(t)$ are referred to as the field autocorrelation function and normalized field autocorrelation function respectively. In equations 2.15 to 2.19, B is the baseline and β is the coherence factor that is generally considered an adjustable parameter in the data analysis procedure. $g_1(t)$ is related to the relaxation function by:

$$g_1(t) = \frac{S(q, C, \tau)}{S(q, C, 0)} \quad (2.22)$$

More detailed information can be obtained from the reference by Kim [Kim, et al., 1990].

For a system consisting of non-interacting homogenous mono-disperse spherical particles, the normalized field autocorrelation function can be represented by the expression:

$$g_1(t) = \exp(-\Gamma t) = \exp\left(-\frac{t}{\tau}\right) \quad (2.23)$$

where τ is the decay time of the process and $\Gamma = \frac{1}{\tau}$ is decay rate. Combining

equation 2.18 with 2.23 results in:

$$G_2(t) = B(1 + \beta \exp(-2\Gamma t)) \quad (2.24)$$

The decay rate is related to the translational diffusion coefficient D through equation:

$$\Gamma = D q^2 \quad (2.25)$$

and Stokes-Einstein expression can be expressed as:

$$D = \frac{kT}{6\pi\eta R_h} \quad (2.26)$$

where k is the Boltzmann constant, T the absolute temperature, η the solvent viscosity and R_h the polymer hydrodynamic radius [Noggle, 1996].

Several decay rates and decay times, Γ_i , τ_i , respectively are present in the system under investigation, thus the field correlation function $g_1(t)$ is the weighted sum of the individual contributions,

$$g_1(t) = \sum w_i \exp(-\Gamma_i t) \quad (2.27)$$

where w_i is the amplitude corresponding to the decay rate, Γ_i . For multiple decay processes, the summation in equation 2.27 can be replaced by an integral, leading to the following expression [Chu, 1991; Brown, 1993]:

$$g_1(t) = \int w(\Gamma) \exp(-\Gamma t) d\Gamma \quad (2.28)$$

where $w(\Gamma)$ is a continuous distribution function of decay rate Γ . If the relationship between $w(\Gamma)$ and Γ is desired, the mathematical transformation needed to obtain such a relationship is rather complex and will not be discussed here. Significant research has been devoted to this field and much success has been achieved and it is now possible to obtain such relationship without much difficulty [Stepanek, 1993].

2.1.2 Theory of Potentiometric and Conductometric Titration

In recent years, much interest has been focused on the self-assembled structured of polyelectrolyte amphiphilic block polymers in aqueous solutions, whereby their characteristics may respond to external stimuli such as pH or the ionic strength of the solution. A number of different experimental techniques e.g. potentiometry, x-ray scattering, viscometry and electrophoretic mobility measurement have been employed to study the association behaviors of polyelectrolyte systems such as polyacrylic acid (PAA), poly(methacrylic acid) (PMAA), and poly(methacrylic acid-co-methylenebisacryamide) microsphere (PMAA microgel) [Mandel et al., 1972; Heitz et al., 1999(a); Heitz et al., 1999(b); Eichenbaum et al., 1998; Eichenbaum et al., 1999(a); Eichenbaum et al., 1999(b)].

Potentiometric and conductometric titrations are commonly used to characterize the association of polyacids. By analyzing the potentiometric and conductometric titration curves, the distribution of the acid groups in the emulsions of polymer can be determined [Heitz et al., 1999(a); 1999(b)]. The potentiometric titration curve is usually treated in terms of the negative logarithm of the apparent dissociation constant ($pK_a = -\log K_a$). For the dissociation of a weak acid in aqueous solution;

The dissociation constant, K_a , is defined by equation;

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (2.29)$$

where $[H^+]$, $[A^-]$ and $[HA]$ are the molarities of free hydrogen ion, counterion, and undissociated acid respectively. The ionization degree of the acid, δ_{HA} is given by the expression;

$$\delta_{HA} = \frac{[A^-]}{[A^-] + [HA]} \quad (2.30)$$

Therefore, the dissociation constant is given by combining equation 2.29 and 2.30;

$$K_a = \frac{\delta_{HA}[H]}{1 - \delta_{HA}} \quad (2.31)$$

For the neutralization reaction, the degree of ionization (δ) is equal to the degree of neutralization (α), hence the negative-logarithm apparent dissociation constant (pK_a) can be expressed by the equation below;

$$pK_a = pH + \log \frac{1 - \alpha}{\alpha} \quad (2.32)$$

By carefully analyzing the curve of pK_a versus neutralization degree (α), the detailed and direct information on the conformational transition can be determined. The investigation of thermodynamic parameters such as Gibbs free energy (ΔG) from titration data had been reported [Gregor et al., 1957; Barone et al., 1974; Dubin et al., 1974; Hirose et al., 1996].

A method of determining ΔG values from the titration data of ionizable polypeptides was described [Zimm and Rice, 1960]. The polymer chains are randomly coiled in their charged state but transformed to a helical structure when the ionizable groups are not charged. The free energy of formation for the α helix structure can be

obtained by applying the equation, $\Delta G = -RT \int \alpha d \ln \alpha_H$, where α_H is the hydrogen ion activity and α is the degree of ionization of the polypeptide [Hermans, 1966].

The required energy to extract proton from poly-acid (ΔG_{el}) is related to the electrostatic potential (Ψ) on the surface of the polyelectrolyte chain if the free energy is only due to the electrostatic interaction [Hirose et al., 1996]. ΔG value was obtained by applying the equation, $\Delta G_{el} = -N_A e \Psi_a$, where N_A is Avogadro's constant, e is the elementary electric charge and Ψ_a is the surface electrostatic potential.

ΔG_{el} may also be expressed by $\Delta G_{el} = \frac{\partial G_{el}}{\partial \nu}$ where G_{el} is the electrostatic free energy of a polyelectrolyte having ν ionized groups. The electrostatic potential Ψ can either be calculated from the solution of Poisson-Boltzmann equation, where the polyelectrolyte chain is treated as an infinite rod.

2.1.3 Theory of transmission electron microscopy

Figure 2.1 Schematic diagram of a Transmission Electron Microscope.

When the electrons encounter the specimen, one of three things can happen. They may pass through it unimpeded. They may be scattered without loss of energy (elastic scattering). Or they may be inelastically scattered; this involves an exchange of energy between the electron beam and the specimen, and may cause the emission from the specimen of secondary electrons or X-rays. Figure 2.1 shows a schematic diagram of a transmission electron microscope.

Image contrast in the TEM depends on preventing the inelastically scattered electrons from contributing to the image. Their exclusion is accomplished by a second small aperture just below the specimen. This is the objective aperture and there are three aperture sizes, which comprise the microscope's contrast control. The specimen is surrounded by the objective lens (not to be confused with the objective aperture), which magnifies the image of the specimen to a small degree, of the order of $\times 50$. Changes to the current flowing through the objective lens constitute the microscope's 'focus' control.

The magnified image from the objective lens is further enlarged by two other lenses below the specimen. They are called the intermediate lens and the projector lens. Both the absolute and relative excitations of these lenses are controlled electronically by a simple 'magnification' control on the microscope's operating console. Most modern TEMs can be set to give a final magnification anywhere in the range $\times 1,000$ – $\times 1,500,000$. Finally, electrons leave the projector lens and strike a screen coated with fluorescent material. The operator sees a continuous image of the specimen, usually green in colour, through a viewing window. Fine adjustments to the image are made while viewing it with an externally mounted, low-power binocular microscope. Brightness, focus, magnification and to some extent contrast are all adjustable. In addition, image quality can be improved by careful adjustments of astigmatism correction controls. However, most of the characteristics of the image are predetermined by techniques used to prepare the specimen. A well-prepared specimen is vital to produce an excellent image.

2.2 Types of Morphologies

The self assembly of small molecule amphiphiles has been studied extensively for a long time [Talmon et al., 1983; Kaler et al., 1989; Schnur et al., 1993; Porter, 1994]. It is believed that results from small molecule amphiphile self-assembly can be applied to the current study on amphiphile block copolymers in dilute solution. Therefore it would be instructive to provide a brief introduction to small molecule self-assembly behaviour.

Usually, a small molecule amphiphile, namely a surfactant, consists of a long straight hydrophobic tail and a small round hydrophilic head. It is the relative sizes of the hydrophobic and hydrophilic part that determine the morphologies of the self assembled aggregates. One reason for the insolubility of the hydrocarbon chain in water is the hydrophobic effect, which is related to the fact that the hydrophobic tail tends to increase the degree of ordering of the water molecules surrounding the hydrocarbon chain [Porter, 1994].

On the other hand, the hydrophilic effect of the head group is believed to be related to a decrease in the order. Both the hydrophobic and hydrophilic effects depend on the structures of the hydrogen bonds near the hydrocarbon chain and the head group and their relative magnitude determines the aqueous solubility of the small molecule amphiphile. When the concentration of the surfactant reaches a critical point, called the critical micellization concentration (CMC), micelles start to form. The reason for the existence of the CMC is due to the fact that in water, the head groups repel one another and the hydrocarbon chains tend to aggregate [Porter, 1994]. A large head

group repulsion and a weak tendency of the hydrocarbon chain to aggregate will result in a high CMC.

Figure 2.2 Schematic illustrations of block copolymer (a) star and (b) crew-cut aggregates.

When diblock copolymers are dissolved in a solvent which is selective for one of the blocks, colloidal size aggregates or micelles can form as a result of the association of the insoluble blocks [Goodman, 1982]. Depending on the composition of the block copolymers, the polarity of the solvent, and the relative solubilities of the blocks in the solvent, the materials can form regular micelle-like aggregates (in aqueous media), which have a hydrophobic core and a hydrophilic corona [Wilhelm et al., 1991; Xu et al., 1993; Astafieva et al., 1993], or aggregates resembling reverse micelles [Desjardins and Eisenberg, 1991; Desjardins et al., 1992; Gao et al., 1992] when the amphiphilic block copolymers are dissolved in a solvent of low polarity. Such assemblies are sometimes referred to as star micelles as shown in Figure 2.2 (a) [Goodman, 1982].

By contrast, if the relative sizes are reversed, the associates are called crew-cut micelles as shown in Figure 2.2 (b) [Halperin et al., 1992; Gao et al., 1994]. The dimension of the core are much larger than those of the corona, as opposed to the star micelles, in which the core is small and the corona is relatively small.

Non-spherical micelles in solutions of block copolymers have also been observed. On the basis of light scattering studies, it was reported that rod-like or cylindrical micelles existed in systems of polystyrene-*b*-poly(methyl methacrylate) in mixed solvents [Utiyama et al., 1974] and polystyrene-*b*-poly(4-vinylpyridine) in dilute solutions [Antonietti et al., 1994], depending on the block copolymer composition. Studies of crew-cut micelles from an asymmetric block copolymer in mixed selective solvents for the short block suggested the existence of block copolymer vesicles [Honda et al., 1994]. The existence of wormlike micelles [Price, 1983] and of platelet aggregates with copolymer cylinders extending from the edges has been proved by direct TEM observation.

The existence of various morphologies in block copolymers in bulk has been known for several years. These morphologies include spheres, rods, lamellae, vesicles, large compound micelles (LCMs), large compound vesicles (LCVs), hexagonally packed hollow hoops (HHHs), and other complicated and inverted structures as shown in Figure 2.3 [Zhang and Eisenberg, 1995; Zhang and Eisenberg, 1996(a); Zhang and Eisenberg, 1996(b); Zhang et al., 1996; Zhang et al., 1997(a); Zhang et al., 1997(b); Yu et al., 1998; Zhang and Eisenberg, 1998; Cameron et al., 1999; Shen et al., 1999].

Figure 2.3 TEM pictures of (a) spherical micelles; (b) vesicles; (c) LCMs; (d) rods; (e) LCVs; (f) HHH. [Zhang and Eisenberg, 1996(a); Zhang and Eisenberg, 1996(b); Zhang et al., 1997(a)].

The morphologies are affected by many factors, namely, the composition of the block copolymer [Zhang and Eisenberg, 1995; Shen and Eisenberg, 2000], the copolymer concentration [Shen and Eisenberg, 1999], the type of common solvent

[Yu and Eisenberg, 1997; Yu et al., 1998], the type and concentration of added ions [Zhang et al., 1996; Zhang and Eisenberg, 1996(a)], and other factors.

As a consequence of the thermodynamics versus the kinetic control during the formation of the aggregates, equilibrium, near equilibrium, and metastable morphologies can be prepared [Zhang et al., 1997(a); Zhang and Eisenberg, 1999]. Spheres, rods, and vesicles can exist as equilibrium morphologies over a range of mixed solvents; and there are regions where two structures coexist in equilibrium. [Shen and Eisenberg, 1999].

On the other hand, under different preparative conditions, near equilibrium and non-equilibrium morphologies such as branched rods, tubules, branched tubules, large compound vesicles, and porous spheres were also isolated [Yu et al., 1996; Cameron et al., 1999]. Besides these morphologies, network structures have also been reported. Fusion of polyelectrolyte micelles into vesicles and fractal toroid-micronetworks had also been observed by increasing polymer and salt concentration [Forster et al., 1999].

More recently, polyelectrolyte fractal growth has been reported [Lee et al., 2004]. Most of the fractal modes of growth [Viscek, 1992] are generally caused by non-equilibrium phenomenon due to interfacial instabilities dominated by the surface tension. Colloidal aggregation [Wang et al, 2000; Puertas et al., 2001], dielectric breakdown [Sheu et al., 1999], electrodeposition [Brady and Ball, 1984; Nanda and Sahu, 2002], dendritic crystal growth [Langer, 1980; Spengler and Coakley, 2003]

and viscous fingering in fluid growth [Daccord, 1986] related to with fractal growth and aggregation phenomenon are the results of the micro and macroscopic aspects of structure formation. Such branched fractal structures, ranging from micro to macroscopic level, display the spontaneous pattern formation in nature [Ball, 1999].

2.3 Fullerene Containing Polymer

Since the discovery of fullerenes, the investigation of fullerene system has been an active research field due to its interesting structure, physical properties, and biological applications [Jensen et al., 1996; Geckeler and Samal, 1999]. Some investigations on the fullerene in non-polar to polar solvents using UV-vis spectroscopy, light scattering and luminescence techniques have been reported [Rudalevige et al., 1998; Nath et al., 1998; Bulavin et al., 2000; Bulavin et al., 2001; Deguchi et al., 2001].

Reversible or irreversible fullerene aggregates with different particle sizes and aggregation numbers could be produced in different solvent systems. Due to the low solubility, use of hazardous solvents, difficult and complicated preparation method, and the poor processability, the use of fullerenes is seriously hampered. To improve the solubility for end-use applications, several methods have been proposed and developed. Because of the doping characteristics of fullerene, it could form charge transfer complex with organic components or polymers through the donor-acceptor interactions, which enhances its solubility in either water or organic solvents [Wang, 1992; William et al., 1995; Sibley et al., 1995; Khairullin et al., 1997; Ungurenasu et al., 2000 ; Sushko et al., 2002; Tarassova et al., 2003; Li and Chen, 2003]. Because

of the strong electron-acceptor properties of fullerene, it could form complex with nitrogen, oxygen and carbonyl functional group on poly(vinyl pyrrolidone), anilines and poly(ethylene-oxide) (PEO) through the charge transfer or electron transfer interaction in aqueous or organic solutions. Water-soluble C₆₀ system can be achieved through the formation of charge transfer complexes of nitrogen containing polymers and C₆₀ using their donor and acceptor properties respectively.

Another way to improve the solubility is to form complexes with surfactants or cyclodextrins through solubilization and encapsulation [Chen and Jenekhe, 1998; Jenekhe and Chen, 1999; Chen and Jenekhe, 1999; Samal and Geckeler, 2000; Filippone et al., 2002]. Fullerene can be partitioned into the micellar core of surfactants through hydrophobic interactions, while cyclodextrin can form either 1:1 or 2:1 complex with fullerenes.

Another possible way to improve the solubility of fullerene is to conjugate the organic components or polymers with fullerene. Connecting fullerene with charged groups such as acidic or basic groups could result in the production of water-soluble fullerene system [Wang et al., 1999; Guldi et al., 1999; Jeng et al., 1999; Felder et al., 2000; Sano et al., 2000; Richardson et al., 2000; Shi et al., 2001; Cerar and Skerjanc, 2003; Shiea et al., 2003]. The self-organization of water-soluble fullerene system in water into vesicles in the scale ranging from nanometer to micrometer were reported as shown in Figure 2.4 [Sano et al., 2000].

Figure 2.4 Schematic drawing showing the contacting regions of two vesicles formed by a novel amphiphilic fullerene derivative with two ammonium headgroups. The double chains are disordered to expose the C_{60} moieties to water molecules, producing hydrophobic force. [Sano et al., 2000].

In aqueous solutions, these fullerene derivatives form nano-scale aggregates through hydrophobic interactions. However, the properties of modified fullerenes will alter depending on the substitution ratio. Grafting of non-chargeable water-soluble groups, such as cyclodextrin and polyethylene glycols can also produce water-soluble fullerenes [Samal and Geckeler, 2000; Tomberli et al., 2000; Angelini et al., 2001; Filippone et al., 2002]. In addition, attempts to produce fullerene anions to increase its solubility were also reported [Sawamura et al., 1997; Zhou et al., 2001]. Zhou and co-workers reported for the first time the production of double layer vesicle from these fullerene anions in aqueous solution as illustrated in Figure 2.5 [Zhou et al., 2001].

Figure 2.5 A bilayer vesicle model. A sector has been cut out for enhanced visibility [Zhou et al., 2001].

Other ways of improving the solubility and processability of fullerene is to graft different types of polymers to fullerene molecules to produce fullerene-containing polymers. Fullerene containing polystyrene and poly(methyl methacrylate) have been synthesized by several research groups [Hawker, 1994; Bunker et al., 1995; Li et al., 2000; Zhou et al., 2000; Ford et al., 2000 Mignard et al., 2002]. Different types of fullerene containing poly(ethylene oxide) were developed and their applications on miscibility were examined [Huang et al., 2000; Jiao et al., 2002; Song et al., 2002; Song et al., 2003(a); Song et al., 2003(b); Goh et al., 2003].

In addition, various types of water-soluble fullerene system were produced by grafting hydrophilic polymer chains to fullerenes [Sun et al., 1999; Okamura et al., 1999; Okamura et al., 2000]. However, most of these studies focused mainly on the synthesis and chemical characterization of the fullerene containing polymers, and very few studies examined their solution behavior [Okamura et al., 1998; Wang et al., 1999; Zhou et al., 2001; Sushko et al., 2001; Song et al., 2003(a); Yang et al.,

2003]. Most of the physical studies on fullerene containing polymer solutions were conducted in organic solvents, such as THF. For C_{60} containing poly(methyl methacrylate) and polystyrene, the C_{60} retains its strong donor-acceptor properties after modification. Core-shell micelles with different aggregation numbers were reported for C_{60} -PMMA and C_{60} -PnBMA in THF solution.

Figure 2.6 TEM pictures of (a) Single- C_{60} -end-capped PEO in water [Song et al, 2003 (a)]; (b) PAA- C_{60} in water [Yang et al., 2003].

The chemical structure and composition of the polymer control the micellization behaviors of C_{60} containing polystyrene in THF. For example, C_{60} -(PS)₂, C_{60} -(PS-PVP)₂ and C_{60} -(PVP)₂ with similar molecular weights formed stable micelles in dilute solution with aggregation number of 1, 6 and 20 respectively. For C_{60} grafted with poly(ethylene oxide)s, large compound aggregates were produced in THF solutions instead of small core-shell micelles as shown in Figure 2.6 (a) [Song et al,

2003 (a)]. By varying the end-capped ratios and molecular weights of PEO, the morphology and association mechanism were altered. For C_{60} capped grafted to both ends of higher molecular weights PEO, gel-like network structure were observed in semi-dilute solutions, resembling that of associative thickeners [Winnik and Yekta, 1997]. A water-soluble C_{60} containing polymer system, i.e. C_{60} -b-PAA, was recently reported [Yang et al., 2003]. C_{60} -b-PAA produced core-shell micelles in aqueous solution as shown in Figure 2.6 (b) and the core-shell structure was found to enhance the photoconductivity of the film.

2.4 Self-assembling Behaviors of Ionic Block Copolymers

By dissolving block copolymers in a selective solvent (i.e. a good solvent for one of the blocks, but a poor one for others), the polymers tend to self-assemble into micellar structure that resembles micelles of normal surfactants. In recent years, much interest has been focussed on the self-assembled structure of polyelectrolyte amphiphilic block copolymers in aqueous solution. The outstanding feature of these polymers is that they self-assemble to form micelles with well-defined size and shape, furthermore, their characteristics may respond to external stimuli such as pH or addition of neutral salt, which makes them useful for specific applications [Urban et al., 1998, Sukhorukov et al., 2001, Sauer et al., 2001]. Thus it is possible to tune the aggregate properties not only by varying the type of monomer, chain length and proportion of the constituting blocks, but also by changing the pH or ionic strength of the solution [Zhang et al. 1999, Sukhorukov et al., 2001, Sauer et al., 2001]. Therefore block copolymers are able to provide more widespread applications than normal surfactants, such as nanoreactors, solubilization of drugs in controlled drug

delivery and potential DNA carriers [Winnik et al., 1997, Hamley et al., 1998, Klok et al., 2001, Benahmed et al., 2001].

The self-assembling of ionic block copolymer is controlled by the amphiphilicity of the polymer together with solvent selectivity. For the case of block polyelectrolytes in aqueous solutions, normally the nonionic (usually hydrophobic) moieties form the core of the micelle surrounded by a corona composed of ionic blocks [Eisenberg et al., 1990]. In addition, due to the high incompatibility between the ionic and nonionic blocks, the micellization occurs at a critical micelle concentration (CMC) as low as $\sim 10^{-8}\text{M}$ [Moffit et al., 1996, Schuch et al., 2000]. Systematic studies on the block polyelectrolyte of poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) and poly(styrene-*b*-methacrylic acid) (PS-*b*-PMAA) with respect to micellar size and structure have been reported [Zhang et al., 1995, Zhang and Eisenberg, 1995]. As proposed by Eisenberg and coworkers, the polymers form star or crew-cut micelles according to the hydrophobicity-hydrophilicity balances between the two blocks [Zhang et al., 1996]. The spherical star micelles consist of a small hydrophobic core surrounded by a relatively large corona, whereas the crew-cut micelles are found when the polymer possesses a large nonionic and hydrophobic block with a short ionic moiety [Eisenberg et al., 1990, Zhang et al., 1995, Zhang and Eisenberg, 1995]. Müller and coworkers reported that polyisobutylene-*b*-poly(methacrylic acid) (PIB-*b*-PMAA) diblock copolymers form core-shell structure with a dense core of PIB blocks and a swollen corona of PMAA blocks [Schuch et al., 2000]. The block copolymers of poly(ethylene glycol) (PEG) based poly(methacrylic acid) (PMAA) derivatives were also found to form pH-dependent core-shell structure, which may offer promising

characteristics for the delivery of charged compounds (i.e. DNA) [Ranger et al., 2001]. Hybrid polymeric micelles with compact polystyrene core and mixed poly(methacrylic acid)/poly(ethylene oxide) shell in 1,4-dioxane(80 vol %)/water have been studied in detail by Stepanec et al. [Stepanec et al., 2001]. Moreover, it was observed that pH and ionic strength strongly affect the CMC values and properties of the micelle. For example, the hydrodynamic radius of micelles of PS-*b*-PMAA increases from ~50nm to ~80nm as pH increases from 4 to 8, resulting from the enhanced electrostatic repulsion upon neutralization of MAA blocks [Moffit et al., 1996].

The micellar conformation of block polyelectrolytes is controlled by a number of contributing factors, i.e. the interactions between solvent molecules with each blocky segment, the interactions between the building blocks and the presence of charge along the polymer chains, thus the polymers may form more complicated micellar structures other than simple core-shell structure. A cylindrical core-shell structure was reported by Müller and coworkers for PS-*b*-PAA block copolymers based on their light scattering and scanning force microscopy studies [Cheng et al., 2001]. Schuch et al. proposed the formation of small vesicle-like structure for poly(isobutylene)-*b*-poly(methacrylic acid) (PIB-*b*-PMAA) in aqueous medium [Schuch et al., 2000]. ABC triblock copolyampholytes of the type poly[5-(N,N-dimethylamino)isoprene]-block-polystyrene-block-poly(methacrylic acid) (AiSA) were found to form large vesicular structure with almost pH-independent radius in aqueous solutions [Bieringer et al., 2000]. The formation of three-layer vesicular micelle from pH responsive triblock copolymer of polystyrene-block-poly(2-

vinylpyridine)-block-poly(ethylene oxide) in water was reported by Gohy et al. [Gohy et al., 2001]. It was also demonstrated that the pH sensitive poly(2-vinylpyridine) shell is useful to tune the size of the vesicle, which is mainly attributed to the electrostatic repulsion between the charged polyelectrolyte chains [Gohy et al., 2001]. Onion-like multilayer micelles were observed in the aqueous solution of block polyelectrolytes based on polystyrene-block-poly(2-vinylpyridine) and poly(2-vinylpyridine)-block-poly(ethylene oxide) by Talingting et al. [Talingting et al., 1999].

Besides the micellar structure, the kinetics of macromolecule exchange between micelle and solution for block polyelectrolyte is another point of interests for many researchers. Eisenberg and coworkers indicated that glassy cores are formed when the nonionic blocks present high T_g (e.g. polystyrene block), which causes extremely low chain mobility and sometimes makes the attainment of equilibrium condition difficult [Moffit et al., 1996]. Tuzar and coworkers reported fluorescence studies on the amphiphilic poly(methacrylic acid)-block-polystyrene-block-poly(methacrylic acid) (PMAA-b-PS-b-PMAA) micelles, where they observe a significant fraction (ca. 20-30%) of the pyrene molecules on or near the polystyrene-water interface, and the diffusion of the probe out of the micelle is the rate-determining step in the release and exchange of large hydrophobes [Cao et al., 1991, Prochazka et al., 1992]. Tuzar et al. also studied the behaviors of di- and triblock copolymers of PMAA and PS in dioxane/water mixtures. When the polymers were dissolved in dioxane-rich mixtures, a dynamic equilibrium between micelles and unimers was observed. But as

the polymers were transferred to water-rich mixtures via dialysis, frozen micelles behaving like autonomous particles were detected [Tuzar et al., 1993].

In the literature, very few studies have been carried out on fullerene containing polymers and there exists a wide range of potential applications to be exploited. The synthesis of fullerene containing poly(*t*-butyl methacrylate) is the precursor to the pH-responsive water-soluble fullerene containing poly(methacrylic acid). A study on the former will provide a better and deeper understanding on the micellization behavior of the latter. Water-soluble fullerene containing polymers are critical and vital in drug delivery applications. So far, very few studies have been conducted on such polymers and detailed study on pH-responsive water-soluble fullerene containing polymers is warranted.

3.0 MATERIALS AND EXPERIMENTAL SECTION

3.1 Polymers Examined In This Study

3.1.1 Synthesis of Fullerene Containing Poly(*tert*-butyl methacrylate)

Figure 3.1 Reaction scheme of PtBMA-*b*-C₆₀.

Synthesis details

In this study, the -Cl terminated PtBMA with narrow molecular weight distribution was first synthesized as reported earlier [Gan et al., 2003]. Using the PtBMA-Cl as macroinitiator, the C₆₀ was grafted in presence of CuCl/HMTETA catalyst system with 1:2 molar ratio of PtBMA-Cl: C₆₀ in 1,2-dichloro benzene at 90°C. After the polymerization, the catalyst was removed by passing through alumina. The unreacted C₆₀ was completely removed by dissolving the polymer in THF and filtered and passed through the alumina column. The filtrate was concentrated and precipitated in excess of water/methanol (1:1) mixture. The procedure was repeated

three times to ensure the complete removal of un-reacted C₆₀. It was found that the average molecular weights (M_n) of PtBMA-*b*-C₆₀ are 8000 g/mol and 14000 g/mol respectively. In addition, the molecular weight distributions as obtained from GPC are 1.2 and 1.22 respectively, indicating only the absence of multi-arms grafted with one C₆₀ molecule.

3.1.2 Synthesis of Fullerene Containing Poly(methacrylic acid)

Figure 3.2 Reaction scheme of PMAA-*b*-C₆₀.

Synthesis details

PMAA-*b*-C₆₀ has been successfully synthesised by atom transfer radical polymerization technique using group protecting chemistry [Zhou et al., 2000]. In this study, well defined -Cl terminated PtBMA was first synthesized as reported earlier [Gan et al., 2003]. Using the PtBMA-Cl (M_n = 16400) as macroinitiator, the

C_{60} was grafted in presence of $CuCl/N,N,N',N',N'',N''$ -hexamethyltriethylenetetramine (HMTETA) catalyst system with 1:2 molar ratio of $PtBMA-Cl : C_{60}$ in 1,2-dichloro benzene at $90^{\circ}C$ for 24h. The number average molecular weight (M_n) of the brown colour solid $PtBMA-b-C_{60}$ determined from GPC is 16,400 Da with $M_w/M_n = 1.2$, indicating the absence of multi-arms grafted with one C_{60} molecule. The covalent attachment of the C_{60} to $tBMA$ was confirmed by UV-Vis spectrophotometer. Finally the *tert*-butyl protecting groups were removed by hydrolyses of the $PtBMA-b-C_{60}$ in presence of $con.HCl/1,4$ -dioxane to give a $PMAA-b-C_{60}$.

3.1.3 Gel Permeation Chromatography

Polymer molecular weights and molecular weight distributions were determined using gel permeation chromatography (GPC). An Agilent 1100 series GPC system equipped with a LC pump, PLgel $5\mu m$ MIXED-C column and RI detector was used. The column was calibrated with narrow molecular weight polystyrene standards. HPLC grade THF stabilized with BHT was used as a mobile phase. The flow rate was maintained at 1.0 ml/min.

The structural formulas of fullerene containing poly(*tert*-butyl methacrylate) and fullerene containing poly(methacrylic acid) are shown in Figure 3.3. The molecular weights and molar mass distribution of the fullerene containing polymers are summarized in Table 3.1.

Figure 3.3 Structural formulas for (A) PtBMA-*b*-C₆₀ and (B) PMAA-*b*-C₆₀.

Polymer	Designation	GPC M _n (Da)	Molar mass distribution
PtBMA- <i>b</i> -C ₆₀	LFBMA	8,000	1.20
PtBMA- <i>b</i> -C ₆₀	HFBMA	14,000	1.22
PMAA- <i>b</i> -C ₆₀	FPMAA	12,500	1.20

Table 3.1 Molecular weights and molar mass distribution of PtBMA-*b*-C₆₀ and PMAA-*b*-C₆₀ copolymers.

3.2 Solvents Used In This Study

Ethyl acetate, chlorobenzene and decalin (from Aldrich Chemical Co.) were used without further purification and they have chemical structure as shown in Figure 3.4.

Figure 3.4 Structural formulas for (A) ethyl acetate and (B) chlorobenzene.

The titrant used in potentiometric and conductimetric titrations is standard 1M NaOH and HCl solutions (from Merck). Water was obtained from the Millipore Alpha-Q water purification system, which has a resistivity of $18.2\mu\text{Ohm-cm}$.

3.3 Equipment and experimental techniques

3.3.1 Light scattering technique

In this study, the Brookhaven laser light scattering system was used. The equipment consists of a BI200SM goniometer (Version 2.0), BI-9000AT digital correlator and other supporting data acquisition and analysis software and accessories. The goniometer system includes focusing optics, a rotating arm, detector optics, detector, neutral density filter, beam focus, sample cell assembly, cells, and a high voltage power supply for the detector. The accessories include a 200 mW 488nm Argon-ion laser, digital temperature controller water bath and the matching liquid filter.

The laser was allowed to warm up for at least 30 minutes at the beginning of each day before any light scattering experiment was carried out. In most experiments, the laser power was adjusted to approximately 100 to 150 mW. In order to improve the accuracy of the measurement, the matching fluid (decahydronaphthalene) was filtered by pumping the fluid through a filter (200 nm) for about 10 minutes. The temperature of the vat and cell was kept constant at the desired temperature using an external water bath.

As the equipment is an optical instrument, the laser must be aligned to reduce measurement errors. In addition, the stability of the laser over the measurement

period must be routinely checked. The stability test, alignment and adjustment of the equipment are explained in details in the equipment manual (Brookhaven Corporation, 1993). The alignment of the laser optics and detectors were checked by measuring the intensities of toluene between 15 and 155 degrees. The averaged intensity at each of the angle were corrected and compared with that at 90 degrees and the deviations were calculated. Good alignment was obtained when the deviation was less than 2%. The alignment and the stability of the optics and the laser were checked every month to ensure that the system is functioning properly. Once this is established, the light scattering system is ready to perform measurements of test solutions. During the measurements, the count rates are controlled by adjusting neutral density filters placed at the incoming laser to reduce the intensity of the laser beam in order to achieve count rates of between 10^5 to 10^6 counts per second. Under such condition, good signal to noise ratio is obtained.

It is known that in light scattering measurements, stray light and dusts are the two major problems that have to be eliminated [Joosten, et al., 1991]. Brookhaven's cell sample cavity is specially designed to minimize stray light by using the matching liquid in the matching vat (Brookhaven Corporation, 1993). If the laser, index matching vat and the sample cell are properly maintained and aligned, stray light does not pose a significant problem. However, dust is a major problem affecting the results and has to be carefully controlled. In light scattering, dust is a generic term assigned to any object that acts as a large scatterer and hence contributes to the output signal. This undesirable signal will affect the quality of the correlation function and in some cases, give rise to spurious results. Most often, dusty samples

limit the reproducibility of the results and give rise to large deviations in the measured values such as the particle diameter. Dust is much more of a problem when using a polar liquid, such as water. A large and sudden jump in the intensity is usually a sign of the presence of dust in the sample. Hence, sample preparation is a critical step that has to be carefully monitored so that the data generated is meaningful. In order to remove the dust, the following steps are necessary during the sample preparation procedure. First, the solvent used for light scattering study should be purified. The water used for the solution preparation was obtained from the Millipore Alpha-Q purification system. The system removes ions and other trace organic materials and particles that are larger than 0.45 μm . Second, the sample cells and other glassware should be cleaned very carefully. All the dirty sample cells were soaked in chromic acid to remove any impurities sticking on the wall of the cell. They were then cleaned using a small brush with soft detergent such as sodium dodecyl sulfate and rinsed thoroughly in tap water followed by several rinses with purified water. Third, filtration and centrifugation were used to remove the dust from the samples. Dusts are usually large particles ($\text{radii} > 1000 \text{ nm}$) and they can be driven to the bottom of the test tubes by centrifugation. All the samples were centrifuged at 3000 rpm for more than 5 hours to remove any dust that may be present in the samples. A BI-SFS sample filtration system was also used to remove dust. The samples were pumped through a 0.2 μm filter at 300 strokes/minute for 20 minutes

The BI-9000AT digital correlator (Ver 1.6) includes the 25ns fixed channels, BI-CON stepping motor controller, PCS analysis software, ISDA size distribution software, IST alignment/stability software, and the BI-ZP Zimm/Berry/Debye plot

software. The digital correlator, which has a maximum channel of 522 and maximum count rate of 40 million counts per second, is considered the heart of the instrument as the raw data is processed and analyzed to yield useful information. This system can be operated automatically or manually in either DOS prompt or in windows mode.

The data obtained from the DLS measurement are the correlation functions represented by either the $G_2(t)$ and $g_2(t)$ function. These functions could then be analyzed using the Inverse Laplace Transform technique to obtain the distribution of decay rate or decay time. The Inverse Laplace Transform analysis method used is REPES (Regularized Positive Exponential Sum).

3.3.2 Potentiometric and Conductometric Titration

The potentiometric and conductometric titrations were conducted using the Radiometer ABU93 Tri-burette Titration System. The instrument is integrated with a standard RS232C interface, where the titration was fully controlled by a computer using the ALIQUOT titration software. The software operates in the Microsoft Excel environment, which allows the user to input adjustable experimental conditions. The electrodes used are Radiometer pHG201 pH glass and Radiometer REF201 reference electrodes. A CDM83 Conductivity Meter was used to measure the change of conductivity during the titration procedure.

All titrations were performed at 25°C (unless otherwise specified) in a titration vessel containing desired amount of polymer solution, and with constant stirring. In the

study of the neutralization behaviors of PMAA-*b*-C₆₀, a 1M NaOH and HCL solution was used as titrants for the forward and back titration, 1 min of lag time was allowed between two dosages to ensure that the reaction has reached equilibrium.

3.3.3 Transmission electron microscopy

A JEOL JEM-2010 transmission electron microscope was used to determine the morphologies of the aggregates formed. It is a multipurpose ultrahigh resolution analytical electron microscope with a wide range of capabilities such as high resolution image observation, microarea X-ray analysis, versatile analysis by convergent-beam electron diffraction, and analysis of the atomic structure and/or bonding state of atoms.

Copper grid precoated with carbon was placed on a filter paper. A drop of polymer solution was placed onto the copper grid and allowed to dry naturally overnight in a desiccator to ensure that the sample was completely dry. Transmission electron microscopy experiments were carried out on the equipment operating at an accelerating voltage of 200 kV.

3.3.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA7 Thermogravimetric Analyzer. PtBMA-*b*-C₆₀ was first dissolved in chlorobenzene, and filtered several times with 0.4 micron filter paper to remove any impurities so as to ensure that only unimers are present in the solutions. TGA was used to determine

the concentration of the PtBMA-b-C₆₀ in chlorobenzene. Temperature was scanned from 25 to 800 °C with a scan rate of 10 °C/min under N₂ flow.

In a thermogravimetric analysis, the percent weight loss of a test sample (polymer solution) is recorded while the sample is being heated at a uniform rate in an appropriate environment. The loss in weight over specific temperature ranges provides an indication of the composition of the sample, which was used to calculate the concentration of the polymer in the solution. TGA was also used to determined the graft rate of fullerene in the fullerene containing polymers

3.3.5 UV-vis Spectroscopy measurements

HP8453 UV-visible spectroscopy equipped with a HP89090A temperature control unit was used to measure the absorption the polymer solutions. For the absorption study, the wavelength was scanned from 200 to 800 nm at 25 °C.

3.3.6 Viscosity measurements

Contraves LS40 controlled rate rheometer was employed to measure viscosity of the ethyl acetate-chlorobenzene mixed solvents at different compositions. It was fitted with the MS 41S/1S concentric cylinder measuring system consisting of a cup (12 mm diameter) and a bob (11 mm diameter) of length 8 mm. All the geometry setups were equipped with a water-circulating bath and peltier plate, to ensure a uniform temperature in the samples. All experiments were conducted under the temperature of 25 °C unless otherwise stated.

3.3.7 $\frac{\partial n}{\partial C}$ measurements

As the concentration of polymer changes, the refractive index of the polymer solutions also changes. This parameter is known as $\frac{\partial n}{\partial C}$, that is, the change of refractive index with respect to concentration. . This value is required as a parameter in molecular weight measurements using light scatterings.

A Brookhaven Instrument refractometer (BI-DNDC) may be used in either static or dynamic mode. In static mode, the specific refractive index increment, $\frac{\partial n}{\partial C}$ is determined. In dynamic mode dn/dc is already known, and the instrument is used as a concentration detector for GPC applications.

In this study, static mode was used to determine the $\frac{\partial n}{\partial C}$ of PtBMA-b-C₆₀ in ethyl acetate-chlorobenzene mixed solvents.

3.3.8 Refractive index measurements

As the solvent composition of the mixed solvents changes, its refractive index also changes. This parameter is important in the calculation of the hydrodynamic radius of the aggregate. The refractive indexes of different solvent mixtures of acetate-chlorobenzene were determined using a Atago Refractometer 3T.

4.0 SELECTIVE SOLVENT INDUCED AGGREGATION BEHAVIOUR OF *PtBMA-*b*-C₆₀* IN CHLOROBENZENE- ETHYL ACETATE MIXTURES

In this study, the aggregation behaviour of fullerene containing poly(*tert*-butyl methacrylate), *PtBMA-*b*-C₆₀* with number-averaged molecular weight (M_n) of 14,000 Da and 8,000 Da (denoted by HFBMA and LFBMA respectively) was examined. Since chlorobenzene (CB) is a good solvent for both *PtBMA* and *C₆₀*, and ethyl acetate (EA) is a selective solvent for only *PtBMA*; *PtBMA-*b*-C₆₀* was first dissolved into CB, and then EA was added to induce the formation of aggregates in the solvent mixtures. *PtBMA-*b*-C₆₀* in CB/EA solvent mixtures will self-assemble to produce interesting morphologies. The resulting microstructure was examined by laser light scattering (LLS) and transmission electron microscopy (TEM). Direct morphological investigation determined by TEM provides images of the aggregates that could be used to validate the microstructure determined from light scattering studies.

4.1 Thermogravimetric Analysis

Thermogravimetric analysis was performed on the polymer to determine the concentration of the polymer in chlorobenzene. A typical thermogravimetric analysis graph was plotted as shown in Fig 4.1.

Figure 4.1 TGA thermograms of PtBMA-*b*-C₆₀ in chlorobenzene.

The compositions of the polymer and solvent are shown in Figure 4.1. Since chlorobenzene has a boiling point of 131°C, it was fully evaporated when temperature reached 131°C, leaving behind the polymer. Thus, the weight percent of the polymer was determined from Figure 4.1. Appropriate amount of ethyl acetate was further added to this polymer to obtain the desired solvent composition.

4.2 Dynamic light scattering studies of PtBMA-*b*-C₆₀

Dynamic light scattering was used to determine the hydrodynamic radius (R_h) of the aggregates formed in chlorobenzene-ethyl acetate mixtures at varying concentrations. In this chapter, fullerene containing poly(*t*-butyl methacrylate) (PtBMA-*b*-C₆₀) of two different molecular weights were studied. PtBMA-*b*-C₆₀ of low and high molecular weights will be denoted as LFBMA and HFBMA respectively.

4.2.1 Scattered intensity of PtBMA-*b*-C₆₀ in chlorobenzene-ethyl acetate mixtures

Chlorobenzene is a common solvent for both fullerene (C₆₀) and poly(*t*-butyl methacrylate) (PtBMA), i.e., it is a good solvent (lyophilic) for both blocks. Therefore, the diblock copolymer will exist as unimers in pure chlorobenzene solvent. Ethyl acetate is a good solvent (lyophilic) for PtBMA, but it is a poor solvent for C₆₀ (lyophobic). Therefore, with the addition of this precipitant, aggregation of the copolymer is expected due to the lyophilic and lyophobic interactions of the diblock copolymer with the mixed organic solvents.

Figure 4.2 shows a typical scattered intensity of PtBMA-*b*-C₆₀ polymer solutions at different solvent compositions. As shown from Figure 4.2, the intensity is rather constant when the ethyl acetate molar composition (X_{EA}) is lower than ~ 0.6 . This indicates that the solution comprises of only single polymer chain or unimer and no aggregation is observed. However, as more ethyl acetate was added to the system, there is a sharp increase in the scattering intensity, indicating the aggregation of individual polymer chains. Therefore, there exists a critical solvent composition where aggregation commences, and we shall define this as critical precipitation composition (CPC) in molar composition of the precipitant in the solvent. The critical precipitant composition (CPC) occurs at $X_{EA} \sim 0.65$ for HFBMA. The decrease in the intensity of HFBMA between $X_{EA} \sim 0.7$ and ~ 0.82 will be discussed in section 4.4.

Figure 4.2 Intensity of 0.7wt% HFBMA in chlorobenzene-ethyl acetate mixtures.

LFBMA has a critical precipitant composition of $X_{EA} \sim 0.2$. This reduction in the CPC is due to the shorter lyophilic chain (PtBMA) of the polymer. The lyophilic and lyophobic interaction is being enhanced and this creates a more favourable condition for the formation of aggregates. Thus, LFBMA is capable of forming aggregates even at low ethyl acetate composition.

4.2.2 q^2 dependence of PtBMA-*b*-C₆₀ in chlorobenzene-ethyl acetate mixtures

Dynamic light scattering measures the instantaneous fluctuations of the scattered light produced by PtBMA-*b*-C₆₀ aggregates. The instantaneous variation of the scattered radiation yields the familiar Doppler shift. By analysing the Doppler shift, the hydrodynamic radius, R_h of the aggregates can be determined. However, the

governing equations behind the analysis assume the polymer aggregations to be non-interacting homogenous mono-disperse spherical particles. Hence, it is required to confirm whether PtBMA-*b*-C₆₀ aggregates follow the above-mentioned assumption.

It can be confirmed using equation 2.25:

$$\Gamma = Dq^2 \quad (2.25)$$

where decay rate $\Gamma = \tau^{-1}$ and τ is the decay time obtained using the GENDIST software, where q is the light scattering vector and D is the translational diffusion coefficient.

The light scattering vector, q was obtained using equation 2.1, where q is defined as the intensity difference at different measure angles.

$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \quad (2.1)$$

where n is the refractive index of the solvent, λ is the wavelength of the incident beam and θ is the measuring angle. When Γ was plotted against q^2 and based on equation 2.25, a linear relationship should be observed and the line passes through the origin.

Figures 4.3 and 4.4 show typical relaxation time distribution curves for 1.4 wt% HFBMA and 2 wt% LFBMA in chlorobenzene-ethyl acetate mixtures measured at different scattering angles respectively. A unimodal distribution was observed for HFBMA in X_{EA} of 0.84.

This indicates that only aggregate is present in the polymer solutions. However, a bimodal distribution was observed for LFBMA in X_{EA} of 0.84, which indicates that unimers and aggregates coexist in the polymer solutions. The fast mode corresponds to the unimer and the slow mode corresponds to the aggregate.

The above results indicate that the block length of PtBMA chain plays a vital role in the determination of the coexistence of unimers and aggregates. The relaxation time distribution obtained from the Laplace inversion of the dynamic light scattering correlation function demonstrates complex state of aggregation in solutions.

Figure 4.3 Relaxation time distribution of 1.4 wt% HFBMA in $X_{EA}=0.84$ at different scattering angles.

Figure 4.4 Relaxation time distribution of 2 wt% LFBMA in $X_{EA}=0.84$ at different scattering angles.

Figure 4.5 q^2 dependence of 1.4 wt% LFBMA in $X_{EA}=0.84$.

Figure 4.6 q^2 dependence of 2 wt% LFBMA in $X_{EA}=0.84$.

Figures 4.5 and 4.6 show the typical plots of Γ versus q^2 of HFBMA and LFBMA in chlorobenzene-ethyl acetate mixtures respectively. The plots of Γ versus q^2 of HFBMA and LFBMA in other solvent mixtures exhibits similar trend. The linear dependence of Γ on q^2 indicates that diffusive species are observed, where the peak observed in HFBMA polymer solutions is attributed to the translational diffusion of larger multi-chain aggregates.

On the other hand, the peak for the fast mode observed in LFBMA polymer solutions is related to the translational diffusion of individual copolymer chains or unimers. The peak for the slow mode is attributed to the translational diffusion of larger multi-chain aggregates.

4.2.3 Concentration dependence of PtBMA-*b*-C₆₀ in chlorobenzene-ethyl acetate mixtures

A concentration dependence of HFBMA and LFBMA in solvent mixtures was examined. Figure 4.7 and 4.8 show the typical relaxation time distribution curves of HFBMA and LFBMA in chlorobenzene-ethyl acetate mixtures at different polymer concentrations respectively.

The peaks of HFBMA in $X_{EA}=0.75$ remain constant and do not shift with changes in the polymer concentration. On the other hand, the two peaks of LFBMA in $X_{EA}=0.75$ also exhibit similar trend. This suggests that the unimers of both the HFBMA and LFBMA associate via the close association mechanism, where the particle size remains constant with increasing copolymer concentration.

Figure 4.7 Relaxation time distribution of HFBMA in $X_{EA}=0.75$ at different polymer concentrations.

Figure 4.8 Relaxation time distribution of LFBMA in $X_{EA}=0.75$ at different polymer concentrations.

Figure 4.9 Illustration of close association model.

Initially the copolymer exists as unimers at copolymer concentration lower than the critical micelle concentration (CMC). When the CMC is reached, the single polymer chains or unimers associate into micelles. Further increase in the copolymer concentration will not produce a larger micelle; instead more micelles are being formed as illustrated in Figure 4.9.

4.2.4 Apparent hydrodynamic radius of PtBMA-*b*-C₆₀ at different polymer concentrations

Through manipulating equation 2.1, 2.25 and 2.26, the apparent hydrodynamic radius R_h can be expressed as;

$$R_h^{app} = \frac{kTq^2\tau}{6\pi\eta} \quad (4.1)$$

where k is the Boltzmann constant, T is the absolute temperature, q is the scattering vector, τ is the decay time, η and is the solvent viscosity. The values of the refractive index and viscosity of the mixed solvents are shown in Table 4.1.

Ethyl acetate molar composition, X_{EA}	refractive index	solvent viscosity(mPas)
1.00	1.371	0.35
0.96	1.379	0.36
0.92	1.385	0.37
0.88	1.392	0.38
0.84	1.399	0.39
0.75	1.414	0.42
0.70	1.420	0.44

Table 4.1 Refractive index and viscosity of the mixed solvents (molar composition) at 25 °C.

Figure 4.10 R_h^{app} of HFBMA in $X_{EA}=0.75$ at different polymer concentrations.

Figure 4.11 R_h^{app} of LFBMA in $X_{EA}=0.75$ at different polymer concentrations.

Equation 4.1 was used to calculate the apparent hydrodynamic radius (R_h^{app}) of the aggregates formed by PtBMA-*b*-C₆₀ in the mixed solvent systems. It is important to note that the values of R_h^{app} obtained from dynamic light scattering and static light scattering respectively, are the apparent values since they were determined at a finite polymer concentration.

Figures 4.10 and 4.11 show the typical plots of R_h^{app} of HFBMA and LFBMA respectively in chlorobenzene-ethyl acetate mixtures at different polymer concentrations. HFBMA and LFBMA in other solvent mixtures exhibit similar trend. It shows very clearly that the values of R_h^{app} are independent of the polymer concentrations.

However, for a true R_h value, two conditions have to be satisfied; i.e.,

- I. Scattering angle, $\theta \rightarrow 0$
- II. Concentration, $C \rightarrow 0$

Condition I is satisfied as shown in Figure 4.5 and 4.6 for HFBMA and LFBMA in mixed solvents respectively, where R_h is independent of the scattering angles as $\square$ is proportion to q^2 . To satisfy condition II, the true value of R_h was determined when concentration tends to zero. By extrapolating the value of R_h to zero concentration, the true R_h was determined. The R_h for HFBMA aggregates in $X_{EA}=0.75$ is 100 nm, and the numerical values of for HFBMA in other solvent mixtures are summarised in Table 4.3.

On the other hand, the R_h of LFBMA unimers and aggregates in $X_{EA}=0.75$ are 4 nm and 85 nm respectively. This shows that PtBMA-*b*-C₆₀ with a longer PtBMA chain will result in the formation of larger aggregate. Furthermore, the block length of PtBMA also determines the coexistence of unimers and micelles. PtBMA-*b*-C₆₀ with a longer PtBMA chain tends to associate to aggregates only, whereas a shorter PtBMA chain leads to the formation of both unimers and aggregates.

4.3 Static light scattering studies of HFBMA in solvent mixtures

Static light scattering measures the time-averaged scattered intensities of HFBMA aggregates at various scattering angles in the solvent mixtures, namely from 20° to 100°, in increments of 10° at 25°C. Five different polymer concentrations were used. Through analysis of the excess scattered intensities, one can determine the z-average radius of gyration, R_g , the weight average molar mass M_w of the aggregates and the second virial coefficient A_2 . A positive A_2 suggests that the solvent is a good solvent for the polymer and vice versa.

The equation for the familiar Zimm plot is shown by equation 2.14.

$$\frac{KC}{R_\theta} \approx \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g^2 \rangle_z q^2 \right) + 2A_2C \quad (2.14)$$

where K is a constant, $K = \frac{4\pi^2 n^2 \left(\frac{\partial n}{\partial C} \right)^2}{N_A \lambda^4}$, C is the copolymer concentration, R_θ is the

Rayleigh ratio, M_w is the weight-average molar mass, θ is the measuring angle. R_g in

this case is root-mean square z-average radius of gyration, q is the light scattering vector and A_2 is the second viral coefficient.

As for the terms in the parameter K , N_A is the Avogadro number, $\frac{\partial n}{\partial C}$ is the specific refractive index increment, n is the solvent refractive index (shown in Table 4.1) and λ is the wavelength of the incident beam. The values of specific refractive index increment $\frac{\partial n}{\partial C}$ of HFBMA in the solvent mixtures are shown in Table 4.2.

Ethyl acetate molar composition, X_{EA}	$\frac{\partial n}{\partial C}$ (ml/g)
0.96	0.09248
0.92	0.09288
0.88	0.09335
0.84	0.09382
0.75	0.09483
0.70	0.09523

Table 4.2 Specific refractive index increment of HFBMA in solvent mixtures at 25°C.

From the Zimm Plot, the following information can be obtained from the analysis of the data, where;

the slope of $[(\frac{KC}{R_\theta})]_{C \rightarrow 0}$ against q^2 yields R_g .

the slope of $[(\frac{KC}{R_\theta})]_{q \rightarrow 0}$ against C yields A_2 .

the extrapolation of $[(\frac{KC}{R_\theta})]_{C \rightarrow 0, q \rightarrow 0}$ yields M_w .

Figure 4.12 Zimm plot of HFBMA in $X_{EA}=0.96$.

Ethyl acetate molar composition, X_{EA}	R_h (nm)	R_g (nm)	(R_h/R_g)	M_w (g/mol)	A_2
0.96	131.0	197.7	1.51	3.08×10^7	3.45×10^{-6}
0.92	125.0	177.2	1.42	2.09×10^7	8.74×10^{-6}
0.88	120.0	171.4	1.43	1.76×10^7	4.42×10^{-6}
0.84	78.0	69.7	0.89	1.50×10^6	9.84×10^{-6}
0.75	100.0	80.1	0.80	2.13×10^6	4.69×10^{-6}
0.70	109.0	89.7	0.82	2.34×10^6	3.82×10^{-5}

Table 4.3 Summary of light scattering results of HFBMA in solvent mixtures at 25°C.

Figure 4.12 shows a typical Zimm plot of HFBMA in chlorobenzene-ethyl acetate mixtures. The two solid lines are the extrapolation to zero concentration and zero angle for the determination of the radius of gyration, R_g and second virial coefficient, A_2 respectively. The molecular weight was determined from the vertical intercept of the two solid lines. Zimm plots of HFBMA in other solvent mixtures shows the same trend.

Table 4.3 summarises the results from static light scattering and the R_h of HFBMA in solvent mixtures obtained from dynamic light scattering. A positive A_2 obtained for all solvent mixtures indicates that HFBMA dissolves well in all the solvent mixtures.

4.4 Aggregation behaviour of HFBMA in solvent mixtures

The values of true R_h and R_g of HFBMA in solvent mixtures are shown in Figure 4.13. Figure 4.14 shows the values R_g/R_h of HFBMA in various solvent mixtures. The value of R_g/R_h determines the conformational structure of the aggregates in solution. However, this value only provides a theoretical prediction on the morphology of the aggregates, and independent confirmation on the final morphology of the aggregates will need to be determined by the transmission electron microscopy (TEM).

The aggregation number, N_{agg} of HFBMA in solvent mixtures is depicted in Figure 4.15, with the inset of Figure 4.2 to illustrate the aggregation behaviour of HFBMA in the solvent mixtures.

The aggregation number is defined as;

$$\text{Aggregation number, } N_{agg} = \frac{M_w(\text{aggregates})}{M_w(\text{unimers})}$$

Figure 4.13 shows the hydrodynamic radius R_h and radius of gyration R_g of HFBMA in various solvent mixtures. The R_h decreases from ~ 110 to ~ 80 nm when EA molar composition increases from 0.7 to 0.84. It then increases sharply to ~ 120 nm at $X_{EA}=0.88$ and to ~ 130 nm at $X_{EA}=0.95$. However, R_g decreases from ~ 90 to ~ 70 nm at EA molar composition from 0.7 to 0.84, but increases sharply to ~ 170 nm at $X_{EA}=0.88$ and it increases gradually to ~ 200 nm at $X_{EA}=0.95$.

Figure 4.13 R_g and R_h of HFBMA in chlorobenzene-ethyl acetate mixtures.

Figure 4.14 R_g/R_h of HFBMA in chlorobenzene-ethyl acetate mixtures.

The curve in Figure 4.14 shows an interesting trend with respect to the observed behaviour of R_h and R_g for HFBMA in various solvent mixtures. R_g/R_h remains essentially constant at ~ 0.8 for EA molar composition ranging from 0.7 to 0.84, but it exhibits a sharp transition at EA molar of between 0.84 to 0.88, where R_g/R_h increase sharply to ~ 1.5 and remain constant thereafter. Such transition signifies a step change in the conformation and compactness of HFBMA aggregates.

We are still unclear on the precise change in the morphology of these aggregates based on the R_g/R_h values of 0.8 and 1.5, and confirmation using transmission electron microscopy will be needed. However, we are certain that the morphologies of HFBMA have changed when the ethyl acetate composition, X_{EA} is increased from

0.84 to 0.88. The conformational change in HFBMA aggregates in the solvent mixtures was further elucidated and confirmed by morphological studies using transmission electron microscopy (TEM).

Figure 4.15 Aggregation number of HFBMA in solvent mixtures. Inset depicts the scattered light intensity of HFBMA.

In order to explain the observed changes in the particle size, we have to examine the aggregation number of HFBMA in these solvent mixtures, and the results are depicted in Figure 4.15, while the inset depicting the scattered intensity of HFBMA. We will first discuss the aggregation behaviour for the HFBMA-mixed solvent systems with R_g/R_h of ~ 0.8 , for ethyl acetate molar composition, X_{EA} ranging from 0.7 to 0.84. At X_{EA} ranging from 0.70 to 0.75, the scattered intensity increases, the aggregation number remains essentially constant, while R_h decreases from ~ 110 to 100 nm (Figure 4.13). Initially the aggregate must be in a swollen state since

chlorobenzene is a good solvent for both blocks (C_{60} and PtBMA), where the solvents are partitioned to the core of the aggregate, which swell the aggregates.

When the amount of poor solvent or precipitant (ethyl acetate) is increased, chlorobenzene molecules are displaced from the core, resulting in a denser core as reflected by the increase in scattered intensity. Negligible change in the aggregation number was observed. When the X_{EA} was increased from 0.75 to 0.84, the R_h of HFBMA decreases to ~ 80 nm, which is accompanied by a reduction in the scattered intensity and aggregation number. Therefore, this reduction in R_h is attributed to the decrease in the aggregation number.

We will now discuss the aggregation behaviour of HFBMA-mixed solvent systems with R_g/R_h of ~ 1.5 , observed for ethyl acetate molar composition, X_{EA} ranging from 0.88 to 0.95. The R_h of aggregates increases from ~ 120 to ~ 130 nm, which is attributed to the increase in the aggregation number. Since ethyl acetate is a poor solvent for C_{60} , addition of this precipitant to the system makes the quality of the solvent poorer for C_{60} , which decreases the polymer-solvent interaction and enhances polymer-polymer interaction. This makes the environment more favourably for the formation of larger aggregates.

4.4.1 Morphologies of HFBMA in solvent mixtures

The morphologies of HFBMA in the solvent mixtures are described in this section. As discussed earlier, the particle size is not affected by the copolymer concentration as they associate via the closed association mechanism.

Figure 4.16 Morphology of 0.5wt% HFBMA in $X_{EA}=0.75$.

Figure 4.17 Morphology of 2.0wt% HFBMA in $X_{EA}=0.88$.

Figure 4.18 Morphology of 1.0wt% HFBMA in $X_{EA}=0.92$.

Figure 4.19 Morphology of 0.8wt% HFBMA in $X_{EA}=0.96$.

Figure 4.20 Close up views of HFBMA in solvent mixtures. (a) 0.5wt% HFBMA in $X_{EA}=0.75$. (b) 2.0wt% HFBMA in $X_{EA}=0.88$. (c) 1.0wt% HFBMA in $X_{EA}=0.92$. (d) 0.7wt% HFBMA in $X_{EA}=0.96$.

The morphologies of HFBMA in chlorobenzene-ethyl acetate mixed solvents are shown in Figures 4.16-4.19. “Dimple-like” and “fractured” spherical aggregates were observed. Figures 4.20a-4.20d compare the close-up views of HFBMA in different CB-EA solvent compositions. The shape of the aggregates has the resemblance of vesicles. We believe that the aggregates are probably that of large compound vesicles

(LCVs), where the shells of the vesicles contain an assembly of individual core shell micelles as illustrated in Figure 4.21. The sizes of the aggregates are more evenly distributed as evident from the narrower relaxation time distribution results.

The aggregate consists of many “dimples” at EA molar composition of 0.75 (Figure 4.19a) and this lies in the range of EA molar composition (0.7 to 0.84) where R_g/R_h is ~ 0.8 . However, the sizes of the “dimples” decrease significantly and become almost negligible in the range of EA molar compositions of between 0.88 and 0.96 (Figures 4.20b-4.20d), where R_g/R_h is ~ 1.5 .

Figure 4.21 Illustration of a large compound vesicle (LCV). Top section has been cut off for clarity.

Since chlorobenzene is a good solvent for C_{60} , the individual micelles are swollen as chlorobenzene molecules are partitioned into the core of the micelles and some could have been incorporated into the hollow cavities of the fullerene particle. During

sample drying for TEM microscopic study, lower boiling point EA evaporates first, followed by CB in the micellar core, which then creates dimple-like patterns on the surface of the dried PtBMA film.

When the content of ethyl acetate increases, the micellar core contains lower amounts of chlorobenzene, which renders the core to be much more compact. This may explain why the dimple-like structure is absent, when R_g/R_h increases from 0.8 to 1.5, since insignificant amounts of chlorobenzene is present in the micellar core. Figures 4.19b-4.19d illustrates the reduction in the dimple size on the surface of the aggregate with the addition of ethyl acetate.

The penetration of CB molecules into the fullerene micellar core alters the core density, which shifts the radius of gyration and the translational diffusion of the aggregates. With more CB molecules, the core becomes denser (since density of hollow fullerene particle and that filled with CB is ~ 1.8 and 2.9 g/cm^3 respectively), it yields a smaller R_g and a larger R_h values. With increasing EA composition, the contribution of chlorobenzene molecules to core density decreases, which results in a larger R_g and smaller R_h , which accounts for the observed increase in R_g/R_h . The formation of LCV is based on the balance between the hydrophobic attractions and the repulsions from PtBMA segments. With increasing EA content to more than 0.85, chlorobenzene molecules are expelled from the micellar core, which increase the hydrophobic interactions. This increases the aggregation number within the LCV, resulting in a corresponding increase in both R_g and R_h values.

Transmission electron microscopy (TEM) micrographs show the morphology of the aggregates in dry state. Initially, some chlorobenzene molecules are present in the core of individual micelles. When the LCVs start to dry, chlorobenzene molecules diffuse to the interface of the P(*t*BMA) film and penetrate through the dried P(*t*BMA) film, thereby producing the “dimple-like structure”. The core of the LCVs is filled with ethyl acetate and possibly some chlorobenzene molecules since ethyl acetate is a poor solvent for C₆₀ and hence does not have an affinity for C₆₀. As the sample on the copper grid began to dry, the shells of the LCVs ruptured due to the evaporation of solvent.

Another possible explanation for the “fractured” LCVs could be due to the surface tension when the solvent vaporises from the LCVs. This will cause the shrinkage of the microstructure, and since the final structure is porous in dry state, it cannot withstand the large force generated from the surface tension and gives rise to the fractured structure.

4.4.2 Proposed aggregation behaviour of HFBMA in solvent mixtures

Figure 4.22 shows the schematic representation of the aggregation behaviour of HFBMA in different composition of solvent mixtures. At ethyl acetate composition lower than the critical precipitant composition (CPC), the copolymer remains as single copolymer chain or unimers. As ethyl acetate (precipitant) exceeds the critical precipitant composition (CPC), aggregation of HFBMA commences. Since chlorobenzene is a good solvent for both blocks, the aggregates are in the swollen state at ethyl acetate molar composition, X_{EA} of 0.7.

Figure 4.22 Schematic diagrams illustrating the aggregation behaviour of HFBMA in solvent mixtures. Figures only show the outer layer of the LCVs.

The “dimple-like structures” are attributed to the partition of chlorobenzene molecules to the individual micelles in the LCVs. As the ethyl acetate molar composition is increased to 0.75, the core of aggregates shrinks, with no change in the aggregation number. At $X_{EA}=0.84$, the particle size decreases, attributed to the decrease in the aggregation number. The R_g/R_h of HFBMA at this ethyl acetate molar composition is ~ 0.8 .

At X_{EA} greater than 0.88, R_g/R_h increases to ~ 1.5 suggesting a change in the morphology of the aggregates, where no chlorobenzene molecules can partition into the core of individual micelles in the LCVs. Thus, the overall morphology is more packed. This is shown by the sharp increase in the aggregation number and scattered light intensity.

4.5 Aggregation behaviour of LFBMA in solvent mixtures

Figure 4.22 shows the hydrodynamic radius, R_h of LFBMA in various solvent mixtures. Static light scattering was not conducted as two types of particles are present in the polymer solutions. The scattered intensity of LFBMA in various solvent mixtures was inserted to depict the aggregation behaviour of LFBMA. As shown in the diagram, unimers of R_h of ~ 4 nm remains constant with the addition of ethyl acetate. However, the R_h of the aggregates decreases from ~ 109 nm at $X_{EA}=0.16$ to 68 nm at $X_{EA}=0.96$. This is accompanied by a gradual increase in the scattered intensity.

Figure 4.23 R_h of LFBMA in chlorobenzene-ethyl acetate mixtures. Inset: Scattered intensity of LFBMA in solvent mixtures.

An interesting trend is noted. The decrease in R_h seems to follow a downward trend on the R_h curve of HFBMA (Figure 4.13), where R_g/R_h is ~ 0.8 and TEM revealed “dimple-like structure” along this region for the HFBMA aggregates. It is clearly shown that LFBMA aggregates do not exhibit any significant morphological change as there is no quantum jump in the R_h values, which is observed in the HFBMA polymer solutions. The R_h of LFBMA aggregates decreases gradually with the addition of ethyl acetate.

4.5.1 Morphologies of LFBMA in solvent mixtures

Transmission electron microscopy (TEM) was performed to determine the morphologies formed by the LFBMA aggregates. LFBMA polymer solutions of $X_{EA}=0.24$ and $X_{EA}=0.84$ were chosen for the study. This is to verify if the LFBMA aggregates exhibit different morphologies at the low and high ethyl acetate molar compositions. The morphologies of LFBMA in these two solvent compositions are shown in Figures 4.24 and 4.25.

The morphologies obtained for LFBMA aggregates at $X_{EA}=0.24$ and $X_{EA}=0.84$ resemble the aggregates shown in Figure 4.16. “Dimple-like” spherical aggregates were observed. As discussed in section 4.3.1, the aggregates are probably that of large compound vesicles (LCVs), where the shells of the vesicles contain an assembly of individual core shell micelles.

Figure 4.24 Morphology of 2wt% LFBMA at $X_{EA}=0.24$.

Figure 4.25 Morphology of 2wt% LFBMA at $X_{EA}=0.84$.

An interesting phenomenon was observed. The size of the “dimple” of LFBMA aggregates at $X_{EA}=0.24$ was relatively larger than ones obtained at $X_{EA}=0.84$. This could further reinforce the explanation in section 4.3.1 whereby the “dimple-like structures” are attributed to the partition of chlorobenzene molecules to the individual micelles in the LCVs. As more ethyl acetate was added to the polymer solutions, chlorobenzene molecules are being expelled from the core of the individual micelles, which leads to a decrease in the “dimple” size.

5.0 AGGREGATION BEHAVIOUR OF pH-RESPONSIVE WATER-SOLUBLE PMAA-*b*-C₆₀ IN AQUEOUS AND SALT SOLUTIONS

In this study, a well-defined fullerene containing poly(methacrylic acid), PMAA-*b*-C₆₀ with number-averaged molecular weight (M_n) of 12,500 Da was obtained through the hydrolysis of fullerene containing poly(*t*-butyl methacrylate) in acidic condition. The polymer was hydrophobic and insoluble at low pH. An increase of pH resulted in the ionization of the carboxylic groups on the polymer backbones, which enhanced its hydrophilicity and solubility in the aqueous medium. The addition of salt alters the electrostatic interaction between the charges of the ionized carboxylate groups and the solvent molecules. This triggers interesting conformational changes in the polymer that leads to the self-assembling of the polymers.

The aggregation behaviour of this pH responsive water-soluble polymer in aqueous and salt solutions was further elucidated using potentiometric titration, dynamic light scattering and transmission electron microscopy.

5.1 Titration studies

Potentiometric and conductometric titration were conducted on 0.2 wt% PMAA-*b*-C₆₀ (denoted as FPMAA) in aqueous solutions. Important parameters such as the degree of neutralization (α), negative logarithm apparent dissociation constant (pK_a) can be determined by analysing the pH curves.

Figure 5.1 pH and conductivity curves of 0.2 wt% FPMAA in aqueous solutions.

The degree of neutralization, α , of the carboxylic groups is defined by;

$$\alpha = \frac{[BASE] + [H^+] - [OH^-]}{C_{COOH}} \quad (5.1)$$

where $[BASE]$, $[H^+]$, and $[OH^-]$ are the molarities of added base, free hydrogen ions and hydroxide ions respectively, and C_{COOH} is the total concentration of methacrylic acid groups expressed in moles per litre.

With this definition, the polyacid is completely neutralized at $\alpha=1$. A potentiometric titration and back titration was performed on PMAA-*b*-C₆₀ in aqueous solution. The concentration of the polymer solution is 0.2wt%. Figure 5.1 shows the pH and conductivity curves plotted against the degree of neutralization degree (α) obtained

from titration of 1 M NaOH and back titration of 1 M HCl into the aqueous solutions of PMAA-*b*-C₆₀.

It is noted that the pH curve for titration (open diamond) exhibits a gentle slope in the α range from ~ 0.1 to 0.3, and the slope becomes steeper with the increasing α until the neutralization process is completed at a well-defined equivalence point of $\alpha=1$. This is represented by a sharp increase in the conductivity as shown in the conductivity curve for titration (open triangle). This is due to the fact that upon neutralization, any addition of base will lead to a further increase in the conductivity. The gentle slope in the α range from ~ 0.1 to 0.3 suggests that the aggregates of the PMAA-*b*-C₆₀ may undergo a structural change in the α range of 0.1 to 0.3.

Figure 5.2 pKa curves of 0.2 wt% FPMAA in aqueous solutions.

Usually a more instructive parameter, the negatively logarithm apparent dissociation constant (pK_a) is used for the potentiometric titration of polyelectrolyte solution, where the pK_a is described by the Henderson-Hasselbalch equation (equation 2.32):

$$pK_a \equiv pH + \log \frac{1-\alpha}{\alpha} \quad (2.32)$$

Figure 5.2 compares the dissociation constant (pK_a) curves of PMAA-*b*-C₆₀ for forward titration with 1 M sodium hydroxide and reverse titration with 1M HCl. The pK_a curve of titration (open diamond) exhibits a negative slope in the range of α from 0.1 to 0.3, which corresponds to the region observed in pH curve plotted in Figure 1. This is attributed to the discontinuous conformational transition of polymer particles in the course of neutralization from the insoluble phase to the micellar phase. This negative slope disappears for the pK_a curve of back titration (close diamond), which indicates that the aggregates of PMAA-*b*-C₆₀ exist in the micellar phase, even when the pH was reduced to the unneutralized point ($\alpha=0$).

5.2 UV-vis spectroscopic studies

UV-vis spectroscopy was also carried out to monitor the absorption of fullerene containing poly(methacrylic acid) in aqueous solution as shown in Figure 5.3. C₆₀ shows an obvious absorption peak at 256 and 330 nm in cyclohexane. For the block copolymers of PMAA-*b*-C₆₀, an absorption peak was observed at 259 nm and 335 nm. The grafting of PMAA onto fullerene could have shifted the peaks slightly higher wavelength.

Figure 5.3 UV-vis. spectra of C_{60} in cyclohexane and PMAA-*b*- C_{60} in aqueous solutions at $\alpha=1$. The insert is the enlarged spectra in the visible region.

The insert shows some difference in absorption spectra in the visible wavelength region. The spectra is less structured and no pronounced maxima were observed, which strongly supports the successfully conjugation of PMAA chains onto C_{60} , which perturbs the conjugated structure and the electronic properties of C_{60} molecules. This is also reinforced by the change in the colour of the solution from purple (C_{60}) to yellow (PMAA-*b*- C_{60}). In addition, no obvious absorption at 514 nm was observed, which indicates that the grafting of PMAA to C_{60} is a 1, 2-addition, and not a 1, 4- addition.

5.3 Dynamic light scattering studies

Dynamic light scattering (DLS) was used to investigate the α and salt effect of PMAA-*b*-C₆₀ in aqueous and salt solutions respectively. This is done by measuring the particle size by varying α values at a fixed polymer concentration, and varying salt (NaCl) concentration at the fully neutralized condition ($\alpha=1$).

Figure 5.4 Relaxation time of 0.2 wt% FPMAA in 0.5 M NaCl at different scattering angles at $\alpha=1$.

Figure 5.4 shows a typical relaxation time distribution function of polymer solution at different scattering angles. FPMAA in other salt and α conditions exhibit the same trend. A bimodal distribution is observed, which indicates that two types of particles coexist. The fast mode corresponds to the micelles and the slow mode corresponds to the bigger aggregates. Each of the distribution functions shifts to a lower relaxation

time with increasing angles. The relaxation time distribution obtained from the Laplace inversion of the dynamic light scattering correlation function demonstrates complex state of aggregation in solutions.

Figure 5.5 q^2 dependence of 0.2 wt% FPMAA in 0.5 M NaCl at $\alpha=1$.

An angle dependence of PMAA-*b*-C₆₀ was investigated. Figure 5.5 shows a typical plot of the dependence of decay rate Γ on q^2 . The linear dependence of Γ on q^2 indicates that the relaxation rates of both peaks are diffusive. The peak for the fast mode is related to the translational diffusion of individual copolymer chains or unimers and the peak for the slow mode is attributed to the translational diffusion of larger multi-chain aggregates. FPMAA in other salt and α conditions exhibit similar trend.

Figure 5.6 Relaxation time distribution of FPMAA at different polymer concentrations in aqueous solutions at $\alpha=1$.

A concentration dependence of PMAA- b -C₆₀ was examined. Figure 5.6 shows a relaxation time distribution of FPMAA at varying polymer concentrations at $\alpha=1$. The same trend was observed in other salt and α conditions. The peaks of FPMAA in aqueous solutions at $\alpha=1$ remain constant with increasing polymer concentrations. This suggests that the unimers of FPMAA associate via the close association mechanism, whereby the particle size remains constant with increasing concentration upon aggregation.

The apparent hydrodynamic radius was determined from the Stokes-Einstein equation:

$$R_h = \frac{kTq^2}{6\pi\eta\Gamma} \quad (4.1)$$

where k is the Boltzmann constant, q is the scattering vector, η is the solvent viscosity, and Γ is the decay rate.

Figure 5.7 R_h^{app} of 0.2 wt% FPMAA in aqueous solutions at $\alpha=1$.

Figure 5.7 shows a typical graph of the dependence of apparent hydrodynamic radius, R_h^{app} plotted against the polymer concentration of 0.2 wt% polymer in aqueous solution at $\alpha=1$. As shown from the figure, the particles sizes correspond to both the fast and slow mode are nearly independent of the polymer concentrations. By extrapolating the value of R_h^{app} to zero concentration, the true hydrodynamic radius, R_h was determined. The particle size which corresponds to the micelles has a R_h of ~ 10 nm. On the other hand, the particle size corresponds to the bigger

aggregates has a R_h of ~ 152 nm. Transmission electron microscopy at the later part of the study revealed that the bigger aggregates are large compound micelles (LCM).

5.3.1 Effect of neutralization degree, α on hydrodynamic radius (R_h)

Figure 5.8 R_h of 0.2 wt% FPMAA in aqueous solutions at varying neutralisation degree, α

Figure 5.8 shows the hydrodynamic radius (R_h) of the particles at different α values. Micelle size of 10 nm remains rather constant throughout the neutralization process, and the size of LCM increases from ~ 90 ($\alpha = 0$) to ~ 152 nm ($\alpha = 1$) with the increase in degree of neutralization, α . LCM comprises of numerous individual small micelles, whereby the fullerene segments of the polymer chains aggregate to form a hydrophobic core of individual micelles; accompanied by a shell consisting of the hydrophilic PMAA segments.

The addition of NaOH neutralizes and ionizes the carboxylic groups of the shell layer, which increases the electrostatic potential on the micellar surface. The shell layer may expand to a certain extent, driven by the electrostatic repulsion between the charged carboxylate groups. Therefore, this increase in the particle size is attributed to the electrostatic repulsion between the ionized carboxylate groups, which leads to the swelling of the aggregates.

5.3.2 Effect of salt on hydrodynamic radius, R_h at $\alpha=1$

Figure 5.9 Relaxation time of 0.2 wt% FPMAA at varying salt concentrations at $\alpha=1$.

The relaxation distribution functions of the polymer solutions at different salt concentrations ($\alpha=1$) are shown in the Figure 5.9. The peak corresponds to the fast

mode remains unchanged with the salt concentration, which indicates that R_h remains constant. On the other hand, the peak corresponds to the slow mode shifts to the left with an increase in salt concentration, indicating a decrease in the R_h .

Figure 5.10 Area ratio of FPMAA aggregates and micelles at different salt concentrations at $\alpha=1$.

It can be seen from Figure 5.9 that as the salt concentration increases, the area under the micelle peak increases, while the area under the aggregate peak decreases. Area under each peak was obtained from the GENDIST software, and it represents the relative scattered intensity contribution of the particle in the solvent. The individual areas were normalised against the total area under the curve and plotted against the concentration as shown above in Figure 5.10. It can be seen from Figure 5.10 that as the amount of salt increases, the normalised area of micelle peak increases and the

normalised area of aggregate peak decreases. Recalling that the scattered intensity is proportional to the sixth power of the particle size, the light scattering technique is very sensitive to large particles. Therefore this may not imply that more micelles and lesser aggregates are formed with the increase of sodium chloride concentration. Instead, the number of micelles and aggregates may remain constant with the addition of sodium chloride.

Figure 5.11 R_h of 0.2 wt% FPMAA at varying salt concentrations at $\alpha=1$.

Figure 5.11 shows the hydrodynamic radius (R_h) of the particle at various NaCl concentrations at fully neutralized condition ($\alpha = 1$). The values of the R_h were obtained by the extrapolation of the apparent R_h of FPMAA to zero concentration at each salt concentrations. The micelle size remains constant at a R_h of 10 nm, and the size of LCM decreases gradually from ~ 152 in the aqueous solution to ~ 105 nm with the addition of 1 M NaCl. The addition of NaCl changes the electrostatic interactions

between the charges of the ions and the solvent molecules. The carboxylate groups are surrounded by a cationic environment with the addition of NaCl, which hinders the association with the water molecules. This leads to the suppression of the electrostatic repulsion between the ionized carboxylate groups, which lead to a more flexible polymer chain. As a result, the particle size decreases.

5.4 Transmission Electron Microscopy (TEM) Studies

Transmission electron microscopy (TEM) was carried out to further investigate the morphology formed by the PMAA-*b*-C₆₀ aggregates. Figure 5.12 presents the phase diagrams of the morphology formed, with the horizontal axis as the NaCl content, and the vertical axis as the neutralization degree ($\alpha=0$ and $\alpha=1$ conditions). Abundance of spherical aggregates were obtained both fully neutralized ($\alpha=1$) and unneutralized ($\alpha=0$) conditions in aqueous solutions (Figures 5.10a, e). The aggregates, believed to be large compound micelles (LCM) are formed as a closer examination on a single aggregate revealed that it comprises of individual smaller spherical aggregates. The sizes of the LCM in the fully neutralized ($\alpha=1$) condition vary from 125-165 nm in radius, and this range is consistent with the DLS measurements. Similarly, size range of 85-120 nm in radius was observed in the unneutralized ($\alpha=0$) condition, which is also consistent with the DLS measurements.

The presence of NaCl at $\alpha = 1$ condition displays an interesting morphology. Fractal pattern was observed when the sample dries up naturally on the copper grid (Figure 5.12b, c). In such isothermal crystallization, the concentration of the diffusing atoms dominates the phenomenon. It is known that the development of such fractal

morphology is governed by a competition between reaction-limited phenomenon or diffusion limited transport and interfacial tension, where any heterogeneous points act as a nucleating point of the following structures. Hence in this case, the LCM acts as the nucleation point for the formation of such fractal pattern. With the addition of more NaCl, the growth of the fractal pattern becomes denser and closely packed together (Figure 5.12c).

However, such fractal pattern was not being observed in the unneutralized condition ($\alpha=0$). Instead, the NaCl crystallizes onto the LCM as shown in Figure 5.12d and 5.12e. The LCM serves as the nuclei for the crystallization of the NaCl. The growth of the crystals becomes denser as more NaCl is present in the system, as this is evident from the TEM micrographs as shown in Figure 5.12e. As no fractal pattern is found in the unneutralized condition, we firmly believe that the negative charge on the surface of the LCM plays a vital role in the fractal growth.

Figure 5.12 Phase diagram of PMAA-*b*-C₆₀. (a) aggregates exist as charged LCM at $\alpha=1$. (b) fractal pattern formed with the addition of NaCl. (c) fractal pattern becomes denser with the addition of more NaCl. (d) aggregates exist as uncharged LCM at $\alpha=0$. (e) salt crystallizes on the LCM. (f) crystallization of the salt becomes denser.

Figure 5.13 Proposed mechanism for the morphology development. (a) in $\alpha=1$, formation of fractal pattern induced by negatively charged surface of the LCM upon drying. (b) in $\alpha=0$, “neutral” LCMs act as nuclei for the crystallization of NaCl.

The proposed formations for the morphology observed in the salt systems at both the neutralized ($\alpha = 1$) and unneutralized ($\alpha = 0$) conditions are shown in Figure 5.13. Figure 5.13a illustrates the process of the fractal formation when the polymer solution dries up at the copper grid. In the fully neutralized condition ($\alpha = 1$), the carboxylate groups are ionized with the addition of NaOH, which results in the negative charge at the surface of the LCM. With the addition of NaCl into the solution, the negative charge at the surface attracts the sodium ions (blue circles) which is positively charge, which in turn attracts the negatively charge chlorine ions (red circles) due to the electrostatic attraction. The ions in the vicinity of the surface will tend to attach themselves onto positions where the attractive forces is the greatest, and they will migrate towards positions were a maximum number of similar particles are located. This results in a fairly high concentration of NaCl at the nearest surroundings of the LCM, which decreases as the ions are further away from the negative charge surface of the LCM. Upon drying, the LCM acts as the immediate nuclei in the system for the crystallization to take place and results in the fractal pattern.

The morphology observed in the unneutralized salt condition is illustrated in Figure 5.13b. The aggregates exist as uncharged LCM in the unneutralized condition in solution. Upon the addition of NaCl, the sodium ions and chlorine ions migrate independent of other ions, and they are homogeneously distributed in the solution. When the water in the polymer solution was evaporated to the point of onset of crystallization on the copper grid, the ions are much closer to one another. With LCM acting as the nucleating point, the ions will migrate rapidly by surface diffusion

towards the position where this nucleus is formed, because very little energy is required for an ion to migrate towards that position. The excess NaCl concentration is then deposited directly onto these nuclei. The microcrystals grow continuously until the final size is attained.

To further confirm that the negative charge at the surface of the LCM is the dominant factor in such fractal formation, TEM studies were performed on the aggregates of fullerene containing poly[2-(dimethylamino)ethyl methacrylate] (DMAEMA-*b*-C₆₀) in NaCl solution at low pH. The surface of the aggregates formed is positive charge at low pH. No fractal pattern was observed, instead, the NaCl crystallizes onto the aggregates (Figure 5.14). This further enhances the fact that the negative charge at the surface is critical for such fractal formation.

Figure 5.14 Morphology of 0.5 wt% DMAEMA-*b*-C₆₀ in 0.5 M NaCl at low Ph.

With the intention to broaden such fractal pattern to other useful applications using the negative charged LCM, TEM was carried out to investigate the morphology formed by the PMAA-*b*-C₆₀ aggregates in 0.5 molar lithium bromide (LiBr) solutions at high pH. The aggregates are negatively charged at high pH condition. TEM studies revealed similar fractal pattern (Figure 5.15).

Figure 5.15 Morphology of 0.2 wt% PMAA-*b*-C₆₀ in 0.5 M LiBr at fully neutralized condition.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

In the first part of the study, the aggregation behaviour of fullerene containing poly(*t*-butyl methacrylate), PtBMA-*b*-C₆₀ of two different molecular weights (M_n) in chlorobenzene-ethyl acetate mixed solvents was studied using thermogravimetric analysis, laser light scattering and transmission electron microscopy. They are denoted as LFBMA (low M_n) and HFBMA (high M_n). We observed a critical precipitant concentration (CPC) where aggregation commences, and no aggregation can be observed when the ethyl acetate composition is lower than CPC. LFBMA exhibits a lower CPC, which implies that a shorter PtBMA chain facilitates the aggregation of PtBMA-*b*-C₆₀ in the mixed solvents.

Dynamic light scattering studies show that the micellization of both HFBMA and LFBMA in mixed solvents occurs via the closed association mechanism, as indicated by negligible change in the hydrodynamic radius, R_h with copolymer concentration. In the HFBMA-mixed solvent systems, R_h of aggregates decreases from ~110 nm (ethyl acetate molar composition, X_{EA} of 0.7) to ~80 nm at X_{EA} =0.84. Beyond a critical solvent composition, it increases sharply to ~120 nm at X_{EA} =0.88 and to ~130 nm at X_{EA} =0.95. The radius of gyration (R_g) and molecular weights (M_w) of HFBMA in solvent mixtures were determined from static light scattering. The value of R_g/R_h increases from 0.8 to 1.5 when the ethyl acetate molar composition, X_{EA} increases from 0.84 to 0.88, indicating a change in the morphology of the aggregates.

In the LFBMA-mixed solvent systems, unimers and aggregates coexist in the mixed solvent systems, indicating that block length of PtBMA chain plays an important role in determining the equilibrium coexistence of unimers and aggregates. Unimers of $R_h \sim 4$ nm remains constant in all solvent mixtures, however the R_h of aggregates decreases gradually from ~ 109 nm at $X_{EA}=0.16$ to 68 nm at $X_{EA}=0.96$ with the addition of ethyl acetate.

The morphology of the aggregates was determined by transmission electron microscopy. “Dimple-like structure” and “broken” large compound vesicles (LCVs) were evident. The “dimple-like structure” is attributed to the partitioning of chlorobenzene molecules into individual micelles in the LCVs. The size of “dimple-like structure” decreases with the addition of ethyl acetate. The “broken” aggregates are attributed to the escape of solvent molecules from the core of the LCVs and the surface tension as the solvent evaporates. The morphology of HFBMA resembles those found in LFBMA. However, the “dimple-like structures” are absent when ethyl acetate molar composition increases from 0.84 to 0.88. This is the critical solvent composition where no chlorobenzene molecules are partitioned to C_{60} micellar core, resulting in a more compact aggregate. The aggregation number increases sharply beyond this critical concentration.

In the second part of the study, the aggregation behaviour of fullerene containing poly(methacrylic acid) (PMAA- b - C_{60}), denoted as FPMAA, in aqueous and salt solutions was studied using potentiometric and conductometric titration, UV-vis spectroscopy, dynamic light scattering and transmission electron microscopy. This

pH-responsive water soluble FPMAA was obtained through the hydrolysis of C₆₀-b-PtBMA in acidic condition.

Dynamic light scattering revealed that micelles and aggregates coexist in the polymer solutions. In the aqueous solutions, micelle size of ~10 nm remains rather constant throughout the process of neutralization. The size of the aggregates increases from ~90 nm ($\alpha=0$) to ~152 nm ($\alpha=1$) with the increase in degree of neutralization, α . This is attributed to the electrostatic repulsion between the ionized carboxylate groups upon the addition of NaOH, which leads to the swelling of the aggregates. In the salt solutions at fully neutralized condition ($\alpha = 1$), the micelle size remains constant at a R_h of 10 nm, and the size of aggregates decreases gradually from ~152 nm in the aqueous solution to ~105 nm with the addition of 1 M NaCl. This is attributed to the suppression of the electrostatic repulsion between the ionized carboxylate groups, which leads to a more flexible polymer chain.

Transmission electron microscopy was used to determine the morphology of the aggregates formed. Large compound micelles (LCMs) were observed from the aqueous polymer solutions at both the unneutralized ($\alpha=0$) and fully neutralized condition). Fractal pattern was observed when sodium chloride (NaCl) is present at $\alpha=1$, and the growth of the fractal pattern becomes closely packed with increase concentration of NaCl. At $\alpha=0$, LCMs act as the immediate nucleation site for the crystallization of NaCl upon evaporation. The growth of the crystals becomes denser as more NaCl is present in the system. Negatively charged surface of the LCMs has been attributed as the dominant factor for such fractal pattern formation

6.2 Recommendations for future work

- ⇒ Transmission electron microscopy is used to confirm the morphology of the aggregates formed in the dry state. Further confirmation the morphologies of the aggregates by freeze-drying techniques should be carried out. Freeze drying can be used to reduce the distortion that occurs when a wet specimen dries by normal evaporation. This distortion is caused by the forces of surface tension going from a liquid to a vapour phase. If the specimen is frozen and maintained in a frozen state and vacuum is applied, the frozen water can be removed by sublimation. This avoids the vapour stage and reduces the distortion.

- ⇒ Block length of PtBMA segment in PtBMA-*b*-C₆₀ chlorobenzene-ethyl acetate mixed solvents plays a vital role in the coexistence of unimers and aggregates, and the morphologies formed by the aggregates. PtBMA-*b*-C₆₀ of different average molecular weights can be synthesized to further elucidate the effect of the block length on the aggregation behaviour of PtBMA-*b*-C₆₀ in the chlorobenzene-ethyl acetate mixed solvents.

- ⇒ In the second part of the study, fullerene was successfully attached to PMAA chain and its aggregation behaviour has been extensively studied. Fullerene containing polymers of different architectures can be synthesized as shown below. Hydrophobic and hydrophilic interactions can be altered by changing the architecture of fullerene and PMAA segment. New insights of the aggregation behaviour can be further elucidated.

Figure 6.1 Two fullerene molecules attached to one PMAA chain.

Figure 6.2 Two fullerene molecules attached to a longer PMAA chain.

Figure 6.3 One fullerene molecule attached to a longer PMAA chain.

Figure 6.4 One fullerene molecule attached with two PMAA chains.

⇒ Fractal pattern has been observed in PMAA-*b*-C₆₀ polymer solutions in the presence of sodium chloride. This is attributed to the negative charge on the aggregates. To further confirm this interesting phenomenon, various fullerene containing poly(acids), e.g. fullerene containing poly(acrylic acid) (PAA-*b*-C₆₀) could be synthesized and studied. The surface of the aggregates formed will be negatively charged upon neutralization. Furthermore, acrylic acid possesses a glass transition temperature (T_g) of 105 °C, which is lower than the T_g of methacrylic acid (124 °C). It would be interesting to investigate the effect of T_g on the aggregation behaviour of fullerene containing poly(acids).

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